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**A TEXT-BOOK OF  
INORGANIC CHEMISTRY  
VOLUME VI. PART I.**



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# A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,  
Carnegie Gold Medallist.

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THE PERIODIC TABLE.\*

PERIOD.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period .	2 He 4.00	1 H 1.008 3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.000	7 N 14.008	8 O 16.000	9 F 19.00	
Second short period .	10 Ne 20.2	11 Na 22.987	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.027	16 S 32.064	17 Cl 35.457	
First long period { Even series long period { Odd "	18 Ar 39.91	19 K 39.096 20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 52.00	25 Mn 54.938	26 Fe 55.845	27 Co 58.933
Second long period { Even series long period { Odd "	36 Kr 83.8	37 Rb 85.47 38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906	44 Ru 101.07	45 Rh 102.905
Third long period .	54 Xe 131.3	55 Cs 132.91	56 Ba 137.33	57 La 138.905	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm 144.912	
Fourth long period .		66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.967	72 Hf 178.49	
Fifth long period { Even series long period { Odd "	86 Rn 222	87 Fr 223	88 Ra 226	89 Ac 227	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu 244.064
Volume in this series of text-books.	1	2	3	4	5	6	7	8	9

\* The International Atomic Weights for 1925 are adopted in this Table.

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EDITED BY  
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,  
CARNEGIE GOLD MEDALLIST.

## VOLUME VI. PART I. NITROGEN.

BY  
EDMUND B. R. PRIDEAUX, AND HERBERT LAMBOURNE,  
M.A., B.Sc. (N.Z.), D.Sc. (LOND.), F.I.C. M.A. (CANTAB.), M.Sc. (LOND.), F.I.C.

With Frontispiece and Illustrations.



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## GENERAL INTRODUCTION TO THE SERIES.

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches : namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned ; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group O, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are

subjects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the Elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen	=	1.00762.	Oxygen	=	16.000.
Sodium	-	22.996.	Sulphur	=	32.065.
Potassium	-	39.100.	Fluorine	=	19.015.
Silver	=	107.880.	Chlorine	=	35.457.
Carbon	=	12.003.	Bromine	=	79.916.
Nitrogen	=	14.008.	Iodine	=	126.920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive,

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii-xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi-xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

June 1928.





## PREFACE.

THE properties of the elements included in Group V. of the Periodic Classification range from those of a typical non-metal, nitrogen, which is entirely devoid of metallic properties, to those of a typical metal, bismuth. In no other part of the Periodic Table is this gradation in properties more clearly seen than in the nitrogen sub-group, the members of which are included in Parts I. and II. of this volume. The volume is completed by Part III., which deals with vanadium, niobium or columbium, and tantalum; protoactinium being dealt with in Volume VII. Part III. Some of these elements have found valuable applications in the steel and electrical industries, for which special purposes they would be difficult to replace. They are of course more typically metallic than arsenic and antimony, but retain the power in their higher oxides of giving salts with alkalis, a property which is thus common to the whole of the group, since it is slightly developed even in bismuth.

Nitrogen and phosphorus in their compounds are essential to life; the element phosphorus is poisonous, while arsenic in its lower valent compounds is one of the most powerful of all inorganic poisons. The poisonous character remains to some extent in antimony, but is lost in bismuth, some compounds of which are used in large quantities in medicine.

Considering now the subject of Part I., nitrogen is unique; it occurs free in enormous quantities in the atmosphere, but is at the same time present only in relatively minute quantities in a state of combination. By causing nitrogen to combine, and thus accomplishing quickly what only happens with extreme slowness in nature, man has increased the possible population of the world to a limit which would have been considered quite unattainable by statistical prophets of the early nineteenth century. Sir William Crookes, in his famous address to the British Association (in 1898), in which he foretold the coming world shortage of combined nitrogen, also adumbrated the remedy, the application of which is told in this volume. In the principal countries of the world great factories have now been established which have removed all danger of a shortage of food due to an insufficient supply of nitrogenous fertilisers. In particular, the Imperial Chemical Industries of Great Britain have a great field open in supplying the needs of agriculture throughout the wide extent of the British Empire, as well as in increasing the somewhat neglected production of food in these Islands by encouraging a suitable form of intensive cultivation.

Nitrogen, under suitable conditions, is a most reactive element, since it will combine, directly or by indirect means, with nearly all

elements—with the metals as nitrides, with hydrogen as ammonia and other compounds, and also with most of the non-metals. With oxygen it yields a range of oxides which differ from one another most conspicuously in their properties and in their modes of preparation. Nitrogen does not enter into combination with either fluorine or bromine alone.

In order to make this volume complete in itself, it has become necessary to include a little subject-matter which is common to other volumes in the Series. Thus a section on the atomic weight of nitrogen has been incorporated from Volume I. The sulphonic derivatives of hydroxylamine, amido-sulphonic acids, etc., as well as the nitrides of sulphur, fall also into Volume VII., Part II. The nitrides, in accordance with the general scheme, are fully described under the metal, etc., concerned, but it was thought desirable to give a general survey of them in this work.

As is usual in this Series, undue detail in physical constants and in the minutiae of chemical processes has been avoided, but abundant references have been given, so that the book may be used as a starting-point for research, or for the compilation of information on particular topics.

Among the books, as apart from original memoirs, which have been most largely consulted are: *The Nitrogen Industry*, Partington and Parker (Constable, 1922); *The Absorption of Nitrous Gases*, Webb (Arnold, 1923); *Ammonia and the Nitrides*, Maxted (Churchill, 1921); as well as works of reference, such as Thorpe's *Dictionary of Applied Chemistry*, and vol. iii, part 3, of the *Handbuch der anorganischen Chemie*, Abegg and Auerbach (1907). Finally, our united thanks are due to the General Editor, Dr. J. Newton Friend, for his helpful criticism and suggestions, and for his great care in the reading of MS. and proofs.

E. B. R. PRIDEAUX.  
H. LAMBOURNE.

UNIVERSITY COLLEGE, NOTTINGHAM,  
June 1928.

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# LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i> . . .	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i> . . .	Annales de Chimie (1719-1815, and 1911+).
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i> . . .	Annales des Mines.
<i>Ann. Pharm.</i> . . .	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i> . . .	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i> . . .	Annalen der Physik (1799-1818, and 1900+).
<i>Ann. Physik, Beibl.</i> . . .	Annalen der Physik, Beiblätter.
<i>Ann. Sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheits- amte</i> . . .	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmac.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles, Genève.
<i>Atti Acc. Torino</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia Lincei.
<i>B.A. Reports</i> . . .	British Association Reports.
<i>Ber.</i> . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i> . . .	See <i>Sitzungsber. K. Akad. Wiss. Berlin</i> .
<i>Ber. Dent. physikal. Ges.</i> . . .	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bot. Zeit.</i> . . .	Botanische Zeitung.
<i>Bul. Soc. Stiinte Cluj.</i> . . .	Buletinul Societății de Științe din Cluj.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. de Belg.</i> . . .	Bulletin de la Société chimique Belgique.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i> . . .	Bulletin de la Société minéralogique de France.
<i>Bull. U.S. Geol. Survey</i> . . .	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie.
<i>Chem. Ind.</i> . . .	Die Chemische Industrie.
<i>Chem. News</i> . . .	Chemical News.
<i>Chem. Weekblad</i> . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . .	Chemiker Zeitung (Cöthen).
<i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Crelle's Annalen</i> . . .	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
<i>Dingl. poly. J.</i> . . .	Dingler's polytechnisches Journal.
<i>Drude's Annalen</i> . . .	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i> . . .	Electrochemical and Metallurgical Industry.



ABBREVIATED TITLE.	JOURNAL.
<i>Eng. and Min. J.</i> . . .	Engineering and Mining Journal.
<i>Gazzetta</i> . . .	Gazzetta chimica italiana.
<i>Gehlen's Allg. J. Chem.</i> . . .	Allgemeines Journal der Chemie.
<i>Geol. Mag.</i> . . .	Geological Magazine.
<i>Gilbert's Annalen</i> . . .	Annalen der Physik (1799-1824).
<i>Giorn. di Scienze Naturali ed Econ.</i> . . .	Giornale di Scienze Naturali ed Economiche.
<i>Helv. Chim. Acta</i> . . .	Helvetica Chim. Acta.
<i>Int. Zeitsch. Metallographie</i> . . .	Internationale Zeitschrift für Metallographie.
<i>Jahrb. kk. geol. Reichsanst.</i> . . .	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
<i>Jahrb. Miner.</i> . . .	Jahrbuch für Mineralogie.
<i>Jahresber.</i> . . .	Jahresbericht über die Fortschritte der Chemie.
<i>Jenaische Zeitsch.</i> . . .	Jenaische Zeitschrift für Naturwissenschaft.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Chem. Soc.</i> . . .	Journal of the Chemical Society.
<i>J. Chim. phys.</i> . . .	Journal de Chimie physique.
<i>J. Gasbeleuchtung</i> . . .	Journal für Gasbeleuchtung.
<i>J. Geology</i> . . .	Journal of Geology.
<i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Metals</i> . . .	Journal of the Institute of Metals.
<i>J. Miner. Soc.</i> . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>J. Pharm. Chem.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physique</i> . . .	Journal de Physique.
<i>J. prakt. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia (Petrograd).
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>Landw. Jahrb.</i> . . .	Landwirtschaftliche Jahrbücher.
<i>Mém. Paris Acad.</i> . . .	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. scient.</i> . . .	Moniteur scientifique.
<i>Münch. Med. Wochenschr.</i> . . .	Münchener Medizinische Wochenschrift.
<i>Nature</i> . . .	Nature.
<i>Nuovo Cim.</i> . . .	Il nuovo Cimento.
<i>Oesterr. Chem. Zeit.</i> . . .	Oesterreichische Chemiker-Zeitung.
<i>Öfvers. K. Vet.-Akad. Forh.</i> . . .	Öfversigt af Kongliga Vetenskaps-Akademins Forhandlingar.
<i>Pflüger's Archiv</i> . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Post</i> . . .	Pharmazeutische Post.
<i>Pharm. Zentr.-h.</i> . . .	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh, and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i> . . .	Physical Review.
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>Pogg. Annalen</i> . . .	Poggendorff's Annalen der Physik und Chemie (1824-1877).
<i>Proc. Chem. Soc.</i> . . .	Proceedings of the Chemical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i> . . .	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Phil. Soc. Glasgow</i> . . .	Proceedings of the Royal Philosophical Society of Glasgow.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Rec. Trav. chim.</i> . . .	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i> . . .	Reports of the Royal Institution.
<i>Schweigger's J.</i> . . .	Journal für Chemie und Physik.

# LIST OF CHIEF ABBREVIATIONS.

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ABBREVIATED TITLE.	JOURNAL.
<i>Sci. Proc. Roy. Dubl. Soc.</i> .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . . .	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i> . . . .	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
<i>Techn. Jahresber.</i> . . .	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Chem. Soc.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Inst. Min. Eng.</i> . .	Transactions of the Institution of Mining Engineers.
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i>	Travaux et Mémoires du Bureau International des Poids et Mesures.
<i>Verh. Ges. deut. Naturforsch. Aerzte.</i> . . . .	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wied. Annalen</i> . . . .	Wiedemann's Annalen der Physik und Chemie (1877-1899).
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i> . . .	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem.</i> . . . .	Kritische Zeitschrift für Chemie.
<i>Zeitsch. Chem. Ind. Kolloid.</i> .	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genuss-m.</i> . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i> . .	Zeitschrift für physikalische Chemie, Stochiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i> . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie.



# TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32-35	...	...	...	4-6	...	5 8	90	...
1	...	36-39	...	...	...	7-9	...	8-11	91	...
2	...	40 43	...	...	...	10-12	...	11-14	92	...
3	...	44-47	...	...	...	13-15	...	14-17	93	...
4	...	48-51	...	...	...	16-18	...	17-20	94	...
1805	...	52-55	...	...	...	19-21	...	20-23	95	...
6	...	56-60	...	...	...	22-24	...	23-26	96	...
7	...	61-64	...	...	...	25-27	...	26-29	97	...
8	...	65-68	...	...	...	28-30	...	29-32	98	...
9	...	69-72	...	...	...	31-33	(1) 1*	33, 34	99	...
1810	...	73-76	...	...	...	34-36	2	35, 36	100	...
11	...	77-80	...	...	...	37-39	3	37, 38	101	...
12	...	81-84	...	...	...	40-42	4	39, 40	102	...
13	...	85-88	...	...	...	43-45	5	41, 42	103	...
14	...	89-92	...	...	...	46-48	6	43, 44	104	...
1815	...	93-96	...	...	...	49-51	(2) 1	45, 46	105	...
16	...	(2) 1-3	...	...	...	52-54	2	47, 48	106	...
17	...	4 6	1, 2	...	...	55-57	3	49, 50	107	...
18	...	7-9	3	...	...	58-60	4	51, 52	108	...
19	(1) 1	10-12	4	...	...	61-63	5	53, 54	109	...
1820	2	13-15	5	...	1-3	64-66	6	55, 56	110	...
21	3	16-18	6	...	4-6	67-69	7	57, 58	111	...
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24	7, 8	25-27	9	7-10	13-15	76	10	63, 64	114	1, 2
1825	9	28-30	10, 11	11-14	16-18	Continued as Pogg. Annalen.	11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19-22		12	67, 68	116	6 8
27	12	34-36	(2) 1, 2	20-23	23-26		13	(2) 1, 2	117	9-11
28	13, 14	37-39	3, 4	24-26	27-30		14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34		15	5, 6	119	15-17

\* First series known as *Bulletin de Pharmacie*.

Year.	Ann. J. Sci.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm. chim.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. scient.	Phil. Mag.	Phil. Trans. Annalen.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	7-8	31-34	...	...	35-38	16	...	...	7, 8	120	18-20	...	...	...
31	19, 20	46-48	...	35-39	...	...	39-42	17	...	...	9, 10	121	21-23	...	...	...
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33	23, 24	52-55	3, 4	44-47	...	...	48-50	19	...	...	2, 3	123	27-30	2	...	...
34	25-27	56-57	5, 6	48-50	...	...	51-54	20	1-3	...	4, 5	124	31-33	...	...	...
1835	28, 29	58-60	7, 8	(2) 1-4	...	1	55-58	21	4-6	...	6, 7	125	34-36	...	...	...
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36	32, 33	64-66	11, 12	9-12	...	4, 5	63-65	23	10-12	...	10, 11	127	40-42	3	...	...
37	34, 35	67-69	13, 14	13-16	...	6, 7	67-70	24	13-15	...	12, 13	128	43-45	...	...	...
38	36, 37	70-72	15, 16	17-20	...	8, 9	71-74	25	16-18	...	14, 15	129	46-48	...	...	...
1840	38, 39	73-75	17, 18	21-24	...	10, 11	75-78	26	19-21	...	16, 17	130	49-51	...	...	...
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1845	48-50	53-56	7, 8	41-44	...	20, 21	95-98	7, 8	34-36	...	26, 27	135	64-66	...	...	...
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48	5, 6	65-68	13, 14	53-56	...	26, 27	107-110	13, 14	43-45	...	32, 33	138	73-75	...	1, 2	...
49	7, 8	69-72	15, 16	57-60	...	28, 29	111-114	15, 16	48-48	...	34, 35	139	76-78	...	2, 3	...
1850	9, 10	73-76	17, 18	61-64	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81	...	3	4, 5
51	11, 12	77-80	19, 20	65-68	...	32, 33	119-122	19, 20	52-54	...	(4) 1, 2	141	82-84	...	4	6, 7
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\* Often referred to by Series : Series 3, vols. 1-16, 1871-1886 ; Series 4, vols. 1-24, 1887-1910 ; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

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Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 30	...	113-116	...	58-60	17, 18	101-104	...	2	1, 2	...	...
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62	...	33, 34	...	121-124	2	64-66	(6) 1, 2	109-112	...	4	5, 6	...	...
63	...	35, 36	...	125-128	2	67-69	3, 4	113-116	...	5	7, 8	...	...
64	...	37, 38	...	129-132	3	(4) 1-3	5, 6	117-120	...	(2) 1, 2	9, 10	...	...
1865	...	39, 40	...	133-136	3, 4	4-6	7, 8	121-124	...	3, 4	11, 12	...	...
66	...	41, 42	...	137-140	4	7-9	9, 10	125-128	...	5, 6	13, 14	...	...
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68	...	45, 46	...	145-148	6	13-15	13, 14	133-136	...	9, 10	17, 18	...	...
69	...	47, 48	...	149-152	...	16-18	15, 16	137-140	...	11, 12	19, 20	...	...
1870	...	49, 50	...	153-156	7	19-21	17, 18	141-144	...	3	21, 22	...	...
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Year.	Compt. rend.	Dingl. poly. J.	Gazetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chim.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh. scient.*	Nature.	Phil. Mag.
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71	161	142-144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145-147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
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81	172	...	...	31, 32, 33	...	...	83, 84	...	12-14	20	...	5, 6	...
82	173	...	...	33, 34	...	1	85, 86	...	15-17	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	...	18-20	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	...	21-23	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	...	24-26	24	...	10, 11	...
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92	183	...	8	50, 51, 52	11	101	12	45-47	31	5	...	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48-50	32	6	1, 2	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51-53	33	7	3, 4, 5	...	23, 24	13-15
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\* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF  
INORGANIC CHEMISTRY.  
VOLUME VI. PART I.



# A TEXT-BOOK OF INORGANIC CHEMISTRY.

## VOL. VI. PART I. NITROGEN.

### CHAPTER I.

#### GENERAL CHARACTERISTICS OF THE ELEMENTS OF GROUP V.

##### COMPARISON WITH GROUPS VI. AND IV.

LIKE Group VI., this group falls into two well-marked divisions, the distinction between which is more clearly defined than in the fourth group.

Group V.	
A. Vanadium Group.	B. Nitrogen Group.
	7 N
	15 P
23 V	
	33 As
41 Nb	
	51 Sb
73 Ta	
	83 Bi
91 UX <sub>3</sub> , Pa	

The two short-period elements, nitrogen and phosphorus, are on the whole more closely allied to the Subgroup B elements, arsenic, antimony, and bismuth. Subgroup A contains vanadium, niobium or columbium, tantalum (eka-tantalum or protactinium), all of which are metals with, however, some non-metallic characters in their higher-valent compounds. Indeed the resemblance, in respect of the physical properties of the elements and the general chemical characters of the compounds, is more close between Subgroups V. A and VI. A than between V. A and V. B. Subgroup V. A contains metals which only melt and volatilise at high temperatures. They do not form definite hydrides. Vanadium yields a great variety of salts and oxides, but in the case of niobium and tantalum the types of valency displayed are not specially numerous, as they are in the corresponding members of VI. A. The lower valent compounds of V. A metals are salts of weak bases. Most of the compounds conform to the

ter- or quinque-valent type. The halides of the latter type have a distinct halanhydride<sup>1</sup> character, and are easily hydrolysed, yielding oxyhalides ROX<sub>3</sub>. The pentavalent oxides when hydrated give weak acids, the

<sup>1</sup> That is, they are similar in properties to the halides of the non-metals, as seen in a compound such as PCl<sub>5</sub>, which may be taken as typical.

salts of which, with alkalis, are of the ortho-, meta-, or pyro-type; there is a close resemblance in this respect between vanadium and phosphorus. In the table, the symbols of the elements are preceded by their atomic numbers, the atomic number of the radioactive elements being deduced from their radioactive succession.

### ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF GROUP V. B.

	Nitro- gen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
Atomic weight .	14.008	31.027	74.96	121.77	209.0
Colour (solid) .	White	Yellow Violet Red Scarlet	Dark grey Yellow	White Metallic Lustre	White Metallic Lustre
Density (solid) .	1.0265	1.83 (yellow) 2.34 (violet)	5.73 (metallic)	6.618	9.781
Atomic volume (solid)	13.6	16.9 (yellow) 13.3 (violet)	14.8	18.2	21.3
Melting-point, ° C.	- 210.5	+ 44.2	Below 800	630	269
Boiling-point, ° C.	- 195.7	+ 287.3	616	1440	1420

### THE NITROGEN SUBDIVISION, WITH SUBGROUP V. B.

**Atomic Weights.**—Phosphorus, arsenic, and antimony constitute a triad,<sup>1</sup> the atomic weight of arsenic (74.96) being nearly the mean of those of the other two, namely, 75.5. The existence of these triads is due to the fact that the atomic weights of successive elements are roughly in arithmetical progression, and that the analogous elements of the second short period and of the odd series of the first and second long periods are separated by two complete symmetrical sections of long periods, namely, sulphur to germanium and chromium to tin. Since the atomic numbers are exactly in arithmetical progression, that of arsenic is the exact mean of those of phosphorus and antimony. Triads are found among the elements of Groups I. to VII., both inclusive, in the second short period, and the second halves (odd series) of the first and second long periods. They are also found between the first halves of the first, second, and third long periods from the zero to the second groups inclusive, *i.e.* until the sequence of the elements is interrupted by the "rare earth" metals. Therefore arsenic, antimony, and bismuth do not form a triad, since the sequence is thus interrupted between antimony and bismuth.

**Mass Spectra and Isotopes.**—The atomic weights of these elements approximate very closely to whole numbers. It has been proved by mass spectra analysis that nitrogen, phosphorus, and arsenic are pure elements, *i.e.* all the atoms have exactly the same mass. Antimony has two isotopes of masses 121 and 123 respectively; the ordinary atomic weight (121.77) being nearly the mean of these. Bismuth again

<sup>1</sup> For the history of triads, see this series, Vol. VII., Part I. (1924), p. 4.

is a "pure" element, the mass spectrum indicating an atomic weight of 209. No elements of the nitrogen subdivision are radioactive; indeed this property is absent throughout the whole group, except in the case of uranium  $X_2$  and protactinium.

**Atomic Volumes.**—The atomic volumes of the elements in their condensed forms (solid or liquid) show a gradual increase with rise of atomic weight. They lie at the top of the lower branch of the ascending parts of the atomic volume-atomic weight curve.

**Physical Properties.**—As in the case of the sixth group, the first member is a typical diatomic gas; the relations between nitrogen and phosphorus are very similar to those existing between oxygen and sulphur.

The initial members of the first three groups, namely,  $F_2$ ,  $O_2$ ,  $N_2$ , show a progressive decrease in boiling-point, the temperatures being  $86^\circ$ ,  $90^\circ$ , and  $77^\circ$  abs. respectively. This sequence is suddenly broken with the highly polymerised elements carbon and boron, which head Groups IV. and III. respectively and are the least volatile of all the elements. In the lowness of its boiling-point nitrogen is only surpassed by neon, b.pt.  $27^\circ$ , hydrogen, b.pt.  $20^\circ$ , and helium, b.pt.  $4.3^\circ$  abs. After nitrogen, the boiling-points of the group subdivision rise sharply through P to Sb and Bi, with a slight maximum at antimony. The melting-points reach their maximum at either antimony or arsenic, that of bismuth being considerably lower.

The crystalline forms of the elements are derived from the two most symmetrical systems, cubic and hexagonal.

**Atomicity of the Gaseous Forms.**—The changes in the atomicities of the elements belonging to the nitrogen subdivision with rise of atomic weight are quite analogous to those which are found in the oxygen subdivision of Group VI. The gaseous molecule, diatomic in the first member, becomes more complex, and then simpler again as we descend the series, until in the case of the last member at high temperatures a monatomic molecule characteristic of the metals is formed. At temperatures slightly above the boiling-point the mean atomicity of the vapours is  $P_4$ ,  $As_4$ ,  $Sb_3$ , and between  $Bi_2$  and  $Bi_1$ . At higher temperatures, as is usual in such cases, dissociation takes place. Thus the gaseous molecules are represented by  $As_2$  at  $1738^\circ C.$ ,  $Sb_2$  at  $1640^\circ C.$ ,  $Bi$  at  $2000^\circ C.$

**Allotropic Forms.**—Allotropy is characteristic of the non-metallic elements. The "active" form of nitrogen (*q.v.*) probably consists of single atoms, or of such associated with a molecule, for example ozone. The allotropy of the solid non-metals is of a different kind; the varieties are more numerous and their transformations more sluggish. This kind reaches its maximum in phosphorus (and sulphur, see Vol. VII., Part II.). The numerous allotropic forms of these elements are supposed to be due to distinct kinds of molecules of different complexity. The equilibria and transformations of these molecular species have been partly elucidated with the aid of the phase rule. The allotropic forms of arsenic also show considerable differences in density and other physical properties, and in chemical reactivity. Such differences have almost disappeared in the case of antimony, although a yellow form is known. Bismuth shows slight differences in density and crystalline form, which are found in the case of many metals.



### Physical and Chemical Properties of Compounds.

The principal types of compounds are summarised in the subjoined table.

#### TYPES OF COMPOUNDS FORMED BY GROUP V. B.<sup>1</sup>

Type.	Nitrogen. N.	Phosphorus. P.	Arsenic. As.	Antimony. Sb.	Bismuth. Bi.
RH <sub>3</sub>	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	(BiH <sub>3</sub> )
..	N <sub>3</sub> H, N <sub>2</sub> H <sub>2</sub> , N <sub>2</sub> H <sub>4</sub>	P <sub>12</sub> H <sub>6</sub> , P <sub>2</sub> H <sub>4</sub>	As <sub>2</sub> H <sub>2</sub>	..	Bi <sub>2</sub> H <sub>2</sub>
R <sub>2</sub> O	N <sub>2</sub> O	(P <sub>4</sub> O)	..	..	..
R <sub>2</sub> O <sub>2</sub>	NO	..	..	..	BiO
R <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>3</sub>	P <sub>4</sub> O <sub>6</sub>	As <sub>4</sub> O <sub>6</sub>	Sb <sub>4</sub> O <sub>6</sub>	Bi <sub>2</sub> O <sub>3</sub>
R <sub>2</sub> O <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	P <sub>2</sub> O <sub>4</sub>	..	Sb <sub>2</sub> O <sub>4</sub>	Bi <sub>2</sub> O <sub>4</sub> *
R <sub>2</sub> O <sub>5</sub>	N <sub>2</sub> O <sub>5</sub>	P <sub>4</sub> O <sub>10</sub>	As <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>5</sub> *
RCl <sub>3</sub>	NOCl	PCl <sub>3</sub>	AsCl <sub>3</sub>	SbCl <sub>3</sub>	BiCl <sub>3</sub>
RCl <sub>5</sub>	..	PCl <sub>5</sub>	AsCl <sub>5</sub>	SbCl <sub>5</sub>	..
ROCl	NOCl	..	AsOCl	SbOCl	BiOCl
ROCl <sub>3</sub>	..	POCl <sub>3</sub>	..	(SbSCl <sub>3</sub> )	..
H <sub>3</sub> RO <sub>3</sub>	..	H <sub>3</sub> PO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub> †	H <sub>3</sub> SbO <sub>3</sub> †	..
or R(OH) <sub>3</sub>	..	..	..	Sb(OH) <sub>3</sub> †	Bi(OH) <sub>3</sub>
HRO <sub>2</sub>	HNO <sub>2</sub>	HPO <sub>2</sub>	HAsO <sub>2</sub> †	HSbO <sub>2</sub> †	BiO(OH)
HRO <sub>3</sub>	HNO <sub>3</sub>	HPO <sub>3</sub>	..	HSbO <sub>3</sub> †	HBiO <sub>3</sub> †
H <sub>3</sub> RO <sub>4</sub>	..	H <sub>3</sub> PO <sub>4</sub>	H <sub>3</sub> AsO <sub>4</sub>	H <sub>3</sub> SbO <sub>4</sub> †	..
R <sub>2</sub> S <sub>2</sub>	N <sub>4</sub> S <sub>4</sub>	(P <sub>4</sub> S <sub>3</sub> )	As <sub>2</sub> S <sub>2</sub>	..	..
R <sub>2</sub> S <sub>3</sub>	..	(P <sub>4</sub> S <sub>7</sub> )	As <sub>2</sub> S <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub>	Bi <sub>2</sub> S <sub>3</sub>
R <sub>2</sub> S <sub>5</sub>	N <sub>2</sub> S <sub>5</sub>	P <sub>2</sub> S <sub>5</sub>	As <sub>2</sub> S <sub>5</sub>	Sb <sub>2</sub> S <sub>5</sub>	..
M <sub>3</sub> R	Mg <sub>3</sub> N <sub>2</sub>	Ca <sub>3</sub> P <sub>2</sub>	Na <sub>3</sub> As	Zn <sub>3</sub> Sb <sub>2</sub>	Mg <sub>3</sub> Bi <sub>2</sub>

The elements, certainly up to and including antimony, and possibly also in the case of bismuth, form definite hydrides of the general formula RH<sub>3</sub>. This sign of non-metallic character is hardly developed in bismuth, which can, however, form organo-derivatives such as trimethyl and triphenyl bismuthine, Bi(CH<sub>3</sub>)<sub>3</sub> and Bi(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, as also methyl bismuthine, (CH<sub>3</sub>—BiH<sub>2</sub>). The other elements form very stable and numerous alkyl and other substituted compounds of the ammonium type, including tetra-substituted ammonium, phosphonium, arsonium, and stibonium bases. Ammonia is formed by direct combination with hydrogen in the presence of a catalyst, and is almost completely dissociated at a high temperature. Phosphine and the other hydrides are not formed by direct union but only by coupled reactions. Their principal physical properties are as follows :—

<sup>1</sup> In some cases the formulae represent molecular weights; when these are unknown the simplest formula is given.

\* Behave as peroxides.

† Degree of hydration indefinite. Probably only monobasic.

‡ Known as salts.

### THE PHYSICAL PROPERTIES OF THE HYDRIDES OF GROUP V. B.

	NH <sub>3</sub> .	PH <sub>3</sub> .	AsH <sub>3</sub> .	SbH <sub>3</sub> .
Boiling-point, ° C. .	-33.5	- 86	- 55	-18
Melting-point, ° C. .	-75	-132.5	-119	-88
Heats of formation (Cals. per mol.) .	+12	+ 11.6	- 36.7	-82 to -85

The power of adding on water, with the production of a base, possessed by ammonia, is lost in the case of phosphine and the subsequent hydrides, although phosphine is still capable of adding on to a strong acid giving phosphonium compounds; as, for example, phosphonium iodide, PH<sub>4</sub>I. The general instability shown by the heat of formation, the temperature at which decomposition occurs, and by many chemical reactions, increases rapidly from phosphine to stibine.

**Oxides.**—Nitrogen combines with oxygen directly, but only to a limited extent; it does not, for example, yield either the pentoxide, N<sub>2</sub>O<sub>5</sub>, or the peroxide, N<sub>2</sub>O<sub>4</sub>, by direct union. These are only obtained by indirect means. Phosphorus combines directly with oxygen, giving both the higher oxide, P<sub>4</sub>O<sub>10</sub>, and the lower oxide, P<sub>4</sub>O<sub>6</sub>. Arsenic, antimony, and bismuth, when burnt in oxygen, give As<sub>4</sub>O<sub>6</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Bi<sub>2</sub>O<sub>3</sub> respectively. In order to obtain the higher oxides of these elements, oxidising agents are required. Data are not available for a complete comparison of the heats of formation. The following figures give the heats of union of gaseous nitrogen, and the remaining elements in the solid state, with gaseous oxygen:—

N <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>6</sub> .	As <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>3</sub> .	Sb <sub>2</sub> O <sub>3</sub> .	Bi <sub>2</sub> O <sub>3</sub> .
13.1	370	219	156.4	166.9	139.2 Cals. per mol.

The heats of formation and of hydration of the oxides reach their maximum in the case of phosphorus. The acids are dehydrated more easily, and the salts derived from these are more readily hydrolysed, as the atomic weights of the elements increase. The oxides of the trivalent and quinquivalent elements when hydrated give the -ous and -ic acids,<sup>1</sup> or are known in salts derived from these. In the case of P, As, Sb, these acids, both -ous and -ic, or their salts, can be classified in the types known as ortho-, pyro-, and meta-, in order of diminishing hydration, the formulæ being analogous to those of the prototypes H<sub>3</sub>PO<sub>3</sub>, H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>, HPO<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub>, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, HPO<sub>3</sub>.

**Halides.**—Direct combination with the halogens does not take place in the case of nitrogen, and the halides, when formed by indirect means, are unstable and explosive. Phosphorus, arsenic, and antimony combine directly with fluorine and chlorine to give both ter- and quinque-

<sup>1</sup> Except in the case of bismuth; the hydroxide of trivalent bismuth being basigenic only, while that of quinquivalent bismuth is only known as an acid in the meta-bismuthates of the alkalis, and as a component of the intermediate oxide, Bi<sub>2</sub>O<sub>4</sub>.

halides. The heats of formation of the halides are less than in the case of the more metallic elements. The resulting compounds are halanhydrides in the case of phosphorus and arsenic, while antimony and bismuth may be regarded as yielding salts of very weak bases, with some halanhydride characters. The heats of formation are as follows:—

$\text{PCl}_3$ .	$\text{AsCl}_3$ .	$\text{SbCl}_3$ .	$\text{BiCl}_3$ .	$\text{PCl}_5$ .	$\text{SbCl}_5$ .
+76.6	71.3	91.4	90.6	109.2	104.9 Cals. per mol.

*Sulphides*.—The sulphides of all the elements in the subgroup, except nitrogen, can be made by direct combination in the dry way. The sulphides of arsenic, antimony, and bismuth can also be precipitated from solution. The two former are really thio-acids uniting with alkaline thio-bases to form salts. The sulphides usually belong to the same valency types as the oxides, the trivalent being the most usual.

#### GENERAL CHARACTERISTICS OF NITROGEN.

Nitrogen alone among the common elements is found almost exclusively in the atmosphere, and only to a relatively minute extent in the solid and liquid "ten-mile" crust. In its mode of occurrence it thus resembles the "inert gases" of the atmosphere, and, like them, is also found in small quantities in gases which issue from hot springs, and dissolved in the ocean. Actually the proportion of nitrogen in the ten-mile crust with atmosphere and hydrosphere is only 0.03 per cent.

The part which it plays in the atmosphere as a diluent gas, inert in ordinary combustions, and its separation by liquefaction and other methods, are fully dealt with in Vol. VII., Part I., of this series.

Although relatively less abundant than, say, a less known element, such as titanium, the billions of tons present in the atmosphere are readily accessible to the transformations of modern chemistry. In a state of combination it is essential to all living organisms, forming as it does 15 to 17 per cent. by weight of proteins. It confers upon them variability of reaction, as carbon confers a certain stability.

The commoner compounds of nitrogen are easily decomposed by the action of micro-organisms, heat, hydrolysis, and the affinity of other elements for the oxygen, *e.g.* of nitrates, or of oxygen for the hydrogen, *e.g.* of ammonia. Nor are these compounds usually formed by natural agencies; both in their formation and their conservation the nitrate deposits of West South America are exceptional. A few nitrides also, such as that of boron (see p. 47, and Vol. IV., in this series), are exceptionally stable under ordinary conditions; but even these will not resist the action of superheated steam, and their decomposition probably accounts for the ammonia present in the steam from some hot springs.

Nitrogen is the diatomic gas of lowest group number,<sup>1</sup> and, like oxygen, it is the only diatomic gas in its group. Its resemblances to oxygen are considerable and its contrast to carbon is extreme. Like oxygen, it forms compounds with all the elements of the first two series except fluorine and the inert gases. Like oxygen, it forms gaseous compounds with carbon, solid compounds with the metals, with boron and silicon, volatile compounds with phosphorus, sulphur, and chlorine. The nitrides are, however, in some cases, *e.g.* those of sodium and

<sup>1</sup> Omitting hydrogen, which in this series is in Group I.

silicon, less defined than the oxides. While oxygen is always the electro-negative part of its compounds, nitrogen is in a few cases, *e.g.* in combination with oxygen and chlorine, the electro-positive part of the molecule.

In the number and valency type of its hydrides it most nearly resembles its congener, phosphorus. Both boron and silicon, and of course carbon, form a greater number of hydrides. Some of the hydrides of nitrogen are unique in that, when hydrated, they form alkalies, *i.e.* the solutions contain hydroxyl ions, and it is noteworthy that the same element also forms a strongly acid hydride, hydrazoic acid.

In the number and valency type of its oxides nitrogen most closely resembles vanadium. The higher oxides are anhydrides which, on hydration, give the strong nitric acid and the weaker nitrous acid. Salts can be formed which contain the hydride cation united with the oxide anion, *e.g.* ammonium nitrate. In this property also nitrogen is unique.

The allotropy of nitrogen is only exhibited in active nitrogen, of which, however, the molecular weight is unknown, and which can only be prepared in much smaller quantities than ozone.

The properties of liquid ammonia are somewhat similar to those of water; both compounds are removed from the ordinary sequence of the hydrides of their respective groups, probably on account of polymerisation. The  $\text{—NH}_2$  radical plays a part very similar to  $\text{—OH}$  in many reactions (see p. 79). Other radicals containing nitrogen which enter into a great variety of reactions are, imido  $\text{=NII}$ , oximido  $\text{=NOII}$ , nitroso  $\text{—NO}$ , nitro  $\text{—NO}_2$ , and diazo  $\text{—N=N—}$ .

The neutral oxides of nitrogen,  $\text{N}_2\text{O}$  and  $\text{NO}$ , are represented according to electronic theories of valency by space formulae similar to those used to represent  $\text{CO}_2$  and  $\text{CO}$  respectively.

The higher oxides,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_5$  are acid anhydrides.

The affinity of hydration, both of the hydrides and of the acid anhydrides, is considerable. In the other members of the group the affinity of hydration of the hydrides is practically zero; while that of the anhydrides reaches its maximum value in the case of phosphorus, is moderate in the case of phosphorous oxide and arsenic pentoxide, and only slight in the case of the other oxides.

## CHAPTER II.

### THE NITROGEN ATOM--VALENCY, STEREO-CHEMISTRY, AND STRUCTURE.

#### The Valency of Nitrogen.

ACCORDING to those fundamental conceptions of valency which are based on the numbers of elements which combine with one another to form stable compounds, the elements nitrogen, phosphorus, arsenic, antimony, and bismuth possess the well-defined valencies of 3 and 5, which have been already illustrated by typical compounds (see also this series, Vol. I., section on "Valency"). The spatial directions in which these valencies are distributed around the central atom have been most fully elucidated in the case of nitrogen, which will therefore be taken as the prototype to which the other elements are already known to conform to some extent.

Isomerism among compounds of trivalent nitrogen of the type

$$\begin{array}{c} a \\ | \\ b-N-c \end{array}$$

will not be found if the valencies are in one plane, but only if they are bent; as, for example, along the edges of a tetrahedron.<sup>1</sup>

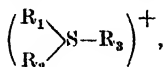
Actually, substituted ammonia bases have not been prepared in isomeric forms (or stereo-isomeric optical antipodes) by any of the usual methods.

It does not follow that the valency directions *are* in the same plane, for the absence of isomerism would be equally well explained by an extreme lability or interchangeability of the occupied positions with the spare valency or "lone pair."<sup>2</sup>

If the nitrogen atom is united to another atom by a double bond, which, as in the case of the ethylenic linkage between two carbon atoms, is incapable of free rotation, a geometrical isomerism becomes possible. The discovery of two isomers of benzildioxime,<sup>3</sup> followed

<sup>1</sup> Van 't Hoff, *Ansichten über die Organische Chemie*, 1878.

<sup>2</sup> Optical activity is found in the case of the tri-substituted sulphonium ion,



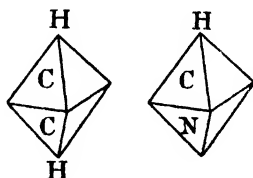
which is quite analogous in constitution, but differs by having a charge which is imparted by one of the radicals R. There must, in this case, be some hindrance to that free interchange of positions which was postulated in the case of the substituted ammonias (see below, "Electronic Theory"). In the case of solid ammonia it has been proved by X-ray analysis that the atoms of hydrogen are in one plane (Mark and Pohland, *Zeitsch. Kristallog.*, 1925, 61, 532).

<sup>3</sup> Goldschmidt, *Ber.*, 1883, 15, 1616, 2170.

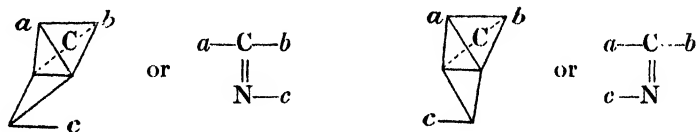
by that of a third form of this compound<sup>1</sup> (see below, p. 12), was first explained by different configurations of the molecules round the singly linked carbon atoms, while the somewhat simpler example of the isomeric  $\alpha$ - and  $\beta$ -benzaldioximes<sup>2</sup> was explained at first as being due to differences in structure. These hypotheses, however, did not agree with further facts, and all such cases of isomerism are now attributed to the spatial configuration of the groups attached to the nitrogen atom.<sup>3</sup>

### Stereochemistry.

Many further proofs have been given of the hypothesis that the three valency directions of the doubly bound nitrogen atom are not coplanar.<sup>4</sup> If we compare with one another the corresponding carbon and nitrogen atoms in acetylene and hydrogen cyanide, also benzene and pyridine, and assume that the three carbon bonds are directed to the angles of a tetrahedron, so also will be those of the nitrogen :



If, now, one pair of bonds is severed, the nitrogen becomes doubly linked, and if the third valency retains its direction, two spatial arrangements result which may be represented by the diagrams or formulæ



e.g. the chloro-benzo-phenone-oximes, by



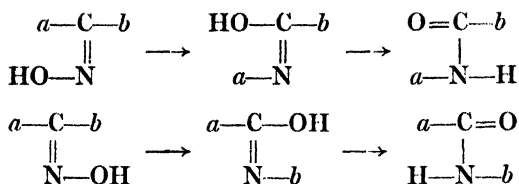
These forms are known as syn- and anti- with respect to the groups "a," according to whether the group "c" is on the same side as, or on the opposite side to, "a." The isomers show differences in physical and chemical properties such as characterise the geometrical isomers derived from ethylene. Their configuration has been discovered by reactions, such as that of Beckmann. When treated with  $\text{PCl}_5$  in benzene or petroleum spirit they are converted into amides, and these with the acids formed by their hydrolysis should be, and are, different in the two cases :

<sup>1</sup> V. Meyer and Auwers, *Ber.*, 1889, 22, 705.

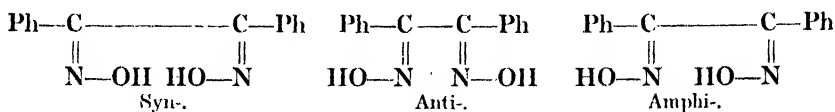
<sup>2</sup> Beckmann, *ibid.*, 1889, 22, 429, 1531.

<sup>3</sup> Hantzsch and Werner, *ibid.*, 1890, 23, 11.

<sup>4</sup> Mills and Miss Bain, *Trans. Chem. Soc.*, 1910, 97, 1866; *ibid.*, 1914, 105, 64.



Finally, it may be mentioned that the dioximes, such as benzildioxime, should exist in three isomeric forms, and this is found to be the case (see above):

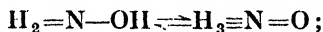


A similar type of isomerism is found in the hydrazones,  $\begin{matrix} a \\ b \end{matrix} \rangle C=N-NHR$ , and osazones. There is also considerable evidence that the diazo-compounds exist in syn- and anti-forms:

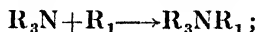


Full details may be obtained from text-books of organic chemistry.

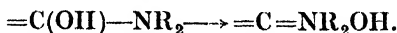
*Change of Valency.*—There are many compounds, such as the ammonium bases, nitric acid, etc., in which it seems impossible or unnatural to retain the trivalency of nitrogen, and the simplest assumption, on the older ideas, is that of quinquivalent nitrogen. In compounds such as nitric acid,  $O_2^-N-OH$ , nitryl fluoride,  $O_2^-N-F$ , the five negative valencies are the contravalencies of Abegg's system (see this series, Vol. I.). Ammonium and substituted ammonium salts are clearly of a different type; of the two extra valencies, one is a positive or hydrogen valency, of the same kind as the first three, and the second is an electrovalency. A change in the valency of nitrogen is exhibited in the tautomerism of hydroxylamine and its derivatives:



also in the formation of ammonium salts and the salts of ammonium bases:



and in the tautomeric change of pseudo-bases into true bases or baso-forms:



It is now no longer necessary, however, to postulate the existence of quinquivalent nitrogen, since all these changes are satisfactorily expressed by the new valency models based on the electronic structure of the atom. Indeed, these theories deny the possibility of quinquivalency of the organic type, *i.e.* quinqu-covalency (see below).

### The Structure of the Nitrogen Atom.

Nitrogen having an atomic number of 7 possesses a nucleus containing 14 protons or units of atomic mass, each carrying unit positive charge, together with 7 electrons, the net positive charge being 7. Closely associated with this are 2 more electrons (K electrons), and in the outer sphere or shell 5 more valency electrons (L electrons). Only this outer shell is represented in the models, which show chemical combination. The model of Kossel,<sup>1</sup> however, shows all the electrons except those which are in the nucleus.

A completed outer shell contains 8 electrons, which in the models of Lewis and Langmuir are symmetrically disposed on the angles of a cube, as in the case of the inert gases. The incomplete shell or "sheath"

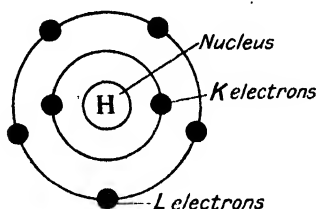


FIG. 1.—Plane model of the nitrogen atom (Kossel).

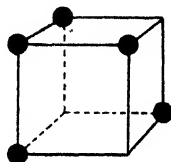


FIG. 2.—Cubic model (Lewis and Langmuir).

of 5 electrons may for convenience also be represented on a cubic model.<sup>2, 3</sup>

**The Electronic Systems of Combined Nitrogen.**—When nitrogen combines with 3 atoms of hydrogen or chlorine, or with 3 univalent radicals, it forms 3 duplet valency bonds, in each of which 1 electron has been contributed by each element. It thus completes the "octet" or stable shell, and may be regarded either as a cube, of which the edges form the bonds, or preferably as a tetrahedron, at the angles of which are situated pairs of electrons. The latter method has the advantage of representing in an intelligible manner a trivalent combination (such as HCN and  $N_2$ ), and of being uniform with the system so successfully adapted to the representation of carbon compounds. The single bond is thus represented by contact at angles, the double by contact along edges, and the triple by contact over faces, of two adjacent tetrahedra. These types will be found in  $F_2$ ,  $O_2$ , and  $N_2$  respectively; and the superior stability or greater inertness of the  $N \equiv N$  molecule may be due to this configuration.

**The Three Kinds of Valency.**—The electronic models of chemical combination have supplied a logical and consistent mode of representing the valencies even of compounds, which could not be so represented by any of the older theories. As nitrogen has always held a central position in the field of discussion, this is perhaps a suitable place in which to summarise the conclusions which have been reached at present.

<sup>1</sup> Kossel, *Ann. Physik*, 1916, 49, 229.

<sup>2</sup> Lewis, *J. Amer. Chem. Soc.*, 1916, 38, 262.

<sup>3</sup> Langmuir, *ibid.*, 1919, 41, 1543.



Historically, the idea of electrovalency as combination with or rejection of the electron was first suggested by Thomson,<sup>1</sup> and more definitely by Ramsay.<sup>2</sup> The explanation of ordinary valency of the organic type as being due to pairs of shared electrons owes much to G. N. Lewis.<sup>3</sup> Finally, the idea of mixed bonds, which is a logical development of electron theories, was developed by Lowry,<sup>4</sup> and some results were stated in the form of postulates by the author<sup>5</sup> as follows, under (3) below. They are particularly helpful in dealing with co-ordination compounds.<sup>6, 7, 8</sup>

The three kinds of valency are :

(1) *Electrovalency*, the electrostatic force which unites the ions of a salt, e.g.  $\text{Na}^+ \dots \text{Cl}^-$ , either in solution or in the solid crystal. Of this kind are the oxygen and halogen valencies of the metals.

(2) *Covalency*, which unites the atoms of non-polar compounds of an organic type, e.g.  $\text{CH}_4$ . Of this kind are the hydrogen valencies of the elements, particularly the non-metals. In this case, each atom shares one or more of its electrons with the other.

(3) *Electro-covalency*, which unites some of the atoms of co-ordinated groups, such as  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $[\text{Co}(\text{NH}_3)_6](\text{NO}_2)_3$ . This mixed bond consists of a pair of electrons, but also produces an internal field of force or latent polarity. This kind of valency also probably unites the non-metals with one another, or with oxygen in the oxy-acids. In this case, two adjacent atoms share as before two electrons, but both electrons are supplied by one only of the sharing atoms.

**Ammonia, Amines, Ammonium Salts, and those of Quaternary Bases.**—Ammonia and other trivalent compounds may be represented as :



in which the scroll divides the electrons which are contributed by each atom.

Nitrogen having completed its octet is now saturated. It still possesses, however, a "lone pair," and, by virtue of this, can attach another atom which lacks an electron, such as the hydrogen ion  $\text{H}^+$ . This carries with it the positive charge, since the whole group, the ammonium ion, has one electron less than the sum of all those required to make all the atoms electrically neutral. Precisely the same reasoning applies to salts of substituted ammonium bases, since  $\text{R}_4$  in  $\text{R}_4\text{X}$  must lose an electron to the halogen X before it can become attached to the nitrogen.

<sup>1</sup> Thomson, "The Corpuscular Theory of Matter" (Constable, 1907).

<sup>2</sup> Ramsay, *Trans. Chem. Soc.*, 1908, 93, 774.

<sup>3</sup> Lewis, "Valence and the Structure of Atoms and Molecules" (Chem. Catalog. Co., 1923), chap. vi.

<sup>4</sup> Lowry, *J. Soc. Chem. Ind. (Chem. and Ind.)*, 1923, 42, 412.

<sup>5</sup> Prideaux, *ibid.*, 1925, 44, 26.

<sup>6</sup> Lowry, *ibid.*, 1923, 42, 224, 316, 412, 462, 672, 711, 746, 1005, 1048.

<sup>7</sup> Spiers, *ibid.*, 1923, 42, 534.

<sup>8</sup> Brockman, *ibid.*, 1924, 43, 756; 1925, 44, 25.



A progressive weakening in the tendency to add  $\text{H}^+$  or  $\text{CH}_3^+$ , etc., and to give “-onium” compounds is shown by the series  $\text{NH}_3$ ,  $\text{NH}_2\text{OH}$ ,  $\text{NCl}_3$ . It is due to the opposing pull on the electrons by the increasingly negative substituent, which thus leaves the nitrogen atom more positive and, therefore, with a less tendency to combine with positive groups. In  $\text{NH}_3$  the nitrogen atom exerts a stronger pull on the common electrons than does a hydrogen atom, as is shown by the fact that in  $\text{NaNH}_2$  the nitrogen has gained a negative electron with formation of a hydrogen ion, which then gains the electron again from the sodium:



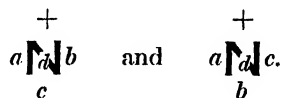
The potentially negative nature of the nitrogen atom thus revealed accounts for the ease with which  $\text{NH}_4^+$ , ammonium ion, is formed. In  $\text{NH}_2\text{OH}$  the oxygen exerts an opposing pull on the common electrons, the nitrogen is less potentially negative, and consequently hydroxylamine salts are formed to a smaller extent, or are more hydrolysed, than ammonium salts.

In chloramine,  $\text{NH}_2\text{Cl}$ , the strongly electro-negative chlorine completely destroys the tendency of the nitrogen to attach itself to positive ions.

**Stereochemistry of Ammonium Derivatives.**—The resolution into optical isomers of compounds of the type  $\text{NabcdX}$  had already been partly effected by Lebel,<sup>1</sup> who, by acting on a solution of methyl-ethyl-propyl-ammonium chloride with the mould “penicillium,” obtained a feebly lævo-rotatory effect on polarised light.

By combining Wedekind’s  $\alpha$ -phenyl-benzyl-allyl-methyl-ammonium iodide with silver d-camphor sulphonate, Pope and Peachey<sup>2</sup> obtained iodides having rotations  $[\alpha]_D$  of  $\pm 66.8$  in chloroform solution.

The various models which have been used to represent the configuration of quinquivalent nitrogen compounds can now be replaced by the simple conception that the ammonium ion is quite analogous to the methane molecule, and the asymmetric nitrogen atom which it contains is dextro- or lævo-rotatory according to the arrangement of the groups  $abc$  when viewed from the fourth angle  $d$ :



**Isosteric Molecules containing Nitrogen.**—Two compounds which can be represented by similar figures containing the same numbers of octets similarly combined are said to be “isosteric.” Such pairs often show a close similarity in physical properties; for example, we have nitrogen and carbon monoxide, nitrous oxide and carbon dioxide. The atoms can be represented by tetrahedra, but it is more convenient to use cubes in cases where this is possible. These are conventionally represented below by formulæ, in which the dots between the atoms represent shared or binding electrons:

<sup>1</sup> Lebel, *Compt. rend.*, 1891, 112, 724.

<sup>2</sup> Pope and Peachey, *Trans. Chem. Soc.*, 1899, 75, 1127.

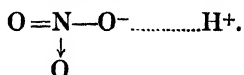


The cyanide and isocyanide ions are also isosteres of carbon monoxide,

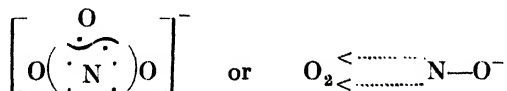


It is not, however, to be expected that these isosteres will all exhibit the same reactivity; for an ion, such as the ammonium ion, is obviously in a different state from methane. Even, however, where the physical state is the same as in CO and N<sub>2</sub>, a closer examination will show differences in the nature of the bonds. Thus, while all three bonds uniting the atoms in the nitrogen molecule may be normal shared duplets, one of the CO bonds must be a "mixed bond." So also in the CO<sub>2</sub> molecules, all the valencies being hydrogen valencies are normal duplets, whereas in N<sub>2</sub>O each nitrogen is united by a normal and by a mixed bond.

*Oxides and Oxy-acids of Nitrogen.*—In all these compounds except N<sub>2</sub>O<sub>3</sub> and HNO<sub>2</sub> the mixed bond must be present. Nitric acid itself is probably a co-ordination compound if represented by the strict octet theory, as:



Since, however, the X-ray examination of crystalline nitrates has shown that the three oxygen atoms are symmetrically placed round the nitrogen,<sup>2</sup> it is usual to represent the nitrogen atom with a sextet instead of an octet of electrons thus:



in the symbols proposed above (p. 15).

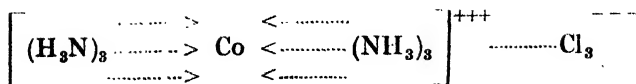
*The Ammines.*—Since the ordinary valencies of nitrogen are saturated in ammonia, this radical is necessarily attached to the central metal atom by mixed bonds, which are thus found to be identical with the "auxiliary valencies," etc., postulated by Werner and others. Indeed, all co-ordination complexes may be shown to contain mixed bonds (see definition (3) above). The numbers of electrons thus added to the central atom are in many cases those required to make up the next stable configuration or zero group gas. As has been pointed out by Lowry,<sup>3</sup> a shortage of one or two electrons may be tolerated, but hardly an excess. Cobalt hexammine chloride is an example of the completion of the stable shell by the addition of "lone pairs" on the ammonia radical.

<sup>1</sup> In these arrangements, which are adopted to save space, it is understood that each of the pairs is shared.

<sup>2</sup> G. N. Lewis, "Valence and the Structure of Atoms and Molecules," 1923, p. 101.

<sup>3</sup> Lowry, *J. Soc. Chem. Ind. (Chem. and Ind.)*, 1923, 42, 318.

Thus in



the cobalt has gained 12 (⊖) from the  $\text{NH}_3$  and lost 3 (⊖) to the halogen atoms, the net gain being 9, which raises its atomic number from 27 to 36, *i.e.* that of krypton.

**Disintegration of the Nitrogen Atom.**—When  $\alpha$ -particles, emitted from radium C or other suitable source, pass through hydrogen and some other gases, they produce a few swiftly moving particles

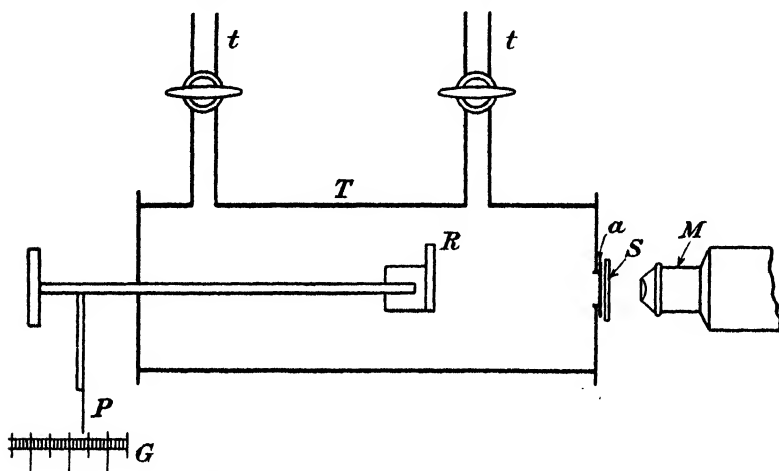


FIG. 3.—Apparatus for effecting and examining the disintegration of the nitrogen atom.

- T*, brass tube.
- t*, *t*, inlet and outlet tubes for gases.
- R*, source of  $\alpha$ -particles.
- a*, absorbing layer of silver foil, etc.
- S*, scintillating screen of zinc sulphide.
- M*, microscope.
- P*, pointer.
- G*, graduated scale for measuring thickness of absorbing air.

which have a range of about four times that of the exciting  $\alpha$ -particles, and which can therefore be detected independently of these by the scintillations which they produce on a screen of zinc sulphide.<sup>1</sup> The later publications of Rutherford and his collaborators, and others, leave no doubt that these particles are “protons,” or hydrogen nuclei, each bearing unit positive charge, which are ejected from the nucleus of an atom by elastic or end-on collisions with the  $\alpha$ -particles.<sup>2</sup> In the case of hydrogen, one collision in about one thousand million produces a swift particle.

The apparatus<sup>2,3</sup> consisted of a tube, containing the gas under

<sup>1</sup> Rutherford, *Phil. Mag.*, 1919, 37, 537, 562, 571, 581.

<sup>2</sup> Rutherford and Chadwick, *ibid.*, 1922, 44, 417; 1921, 42, 809; see also Rutherford, *ibid.*, 1914, 27, 488; Darwin, *ibid.*, 499; Marsden, *ibid.*, 824; Marsden and Lansberry, *ibid.*, 1915, 30, 200; see also Chadwick and Bieler, *ibid.*, 1921, 42, 923; Bieler, *Proc. Roy. Soc.*, 1924, A105, 434.

<sup>3</sup> Rutherford, *Trans. Chem. Soc.*, 1922, 121, 400.

examination, in which is fixed a plate bearing the radioactive preparation, and at one end opposite to this a brass plate, in the centre of which is cut a small opening which is closed by a thin plate of metal, such as silver, aluminium, or iron, whose stopping power for the  $\alpha$ -particles lies between 4 and 6 cm. of air. The zinc sulphide screen is placed opposite the opening outside the tube and distant 1 or 2 mm. from the metal covering. A small portion of the screen, about 2 mm. in diameter, is viewed by a microscope which has a magnification of about 40. The tube is encircled by the poles of an electro-magnet, which deflects the swift  $\beta$ -rays or negative electrons away from the screen.

In this apparatus, hydrogen, and then other elements and compounds have been tested for the emission of swift particles of long range. The

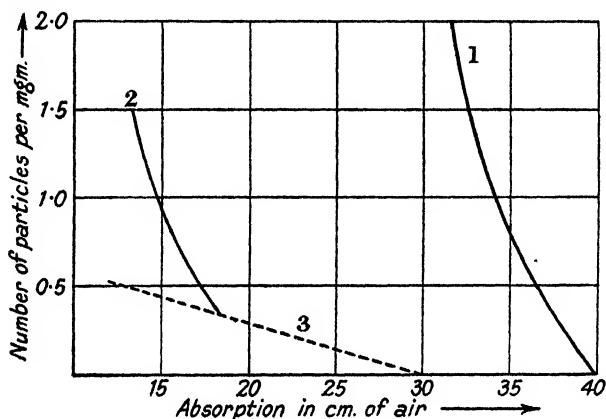


Fig. 4.—Absorption of H-particles derived from nitrogen and hydrogen.

Curve 1. Particles from nitrogen forward.  
 " 2. Particles from nitrogen backward.  
 " 3. Particles from hydrogen.

following description is quoted mainly from one of Rutherford's papers :<sup>1</sup> When the hydrogen is replaced by dry oxygen or carbon dioxide there are still a few scintillations which were believed to be due to traces of hydrogen. The number of scintillations was increased three to four times by substituting air in the tube, and in a greater proportion by pure nitrogen. When  $\alpha$ -particles having a uniform range of 7 cm. of air are employed, the swift particles derived from hydrogen have a range of just under 30 cm., and no scintillations can be detected after absorption by this thickness of air or an equivalent thickness of other absorbing substance. The particles from nitrogen, however, can be detected after an absorption of 40 cm. of air or its equivalent. Those between 30 and 40 cm. cannot, therefore, be ascribed to traces of hydrogen or its compounds which might be present in the nitrogen. These particles are deflected by a magnetic field like the H-particles, with which they appear to be identical in all respects except in velocity and range. Their maximum velocity is  $1.6 v$ , where  $v$  is the velocity of the  $\alpha$ -particle. Some are ejected in a direction contrary to that of the bombarding  $\alpha$ -particles ; the maximum backward range being 18 cm. The number emitted in

<sup>1</sup> Rutherford, *loc. cit.*

all directions by a million  $\alpha$ -particles of range 8.6 cm. is about 20. The same particles can be emitted from the nuclei of other elements (see below), and in particular phosphorus, which gives about the same number as nitrogen under the same conditions, but of a greater range, equal to 65 cm. of air. No element of higher atomic weight than phosphorus was found to give the swift H-particles.

It has been calculated that the chance of liberation of an H-particle from nitrogen is not more than  $\frac{1}{50}$ th of the chance of liberating one from hydrogen in corresponding motion. The  $\alpha$ -particle has to penetrate more deeply into a more complicated system of electrons in the former case. That such a penetration may also cause a *backward* ejection was shown by the simple sketch reproduced from Rutherford's paper.<sup>1</sup> Certain conclusions as to the structure of the atomic nuclei have been

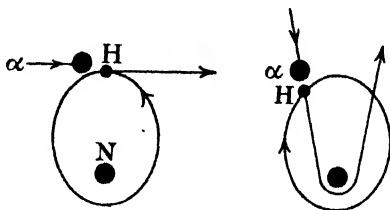


FIG. 5.—Production of swift H-particles from the nitrogen atom (after Rutherford).

drawn from these results. In the first place, it is noticed that H-particles are only liberated from elements the atomic weights of which are given by the series:  $A=4n+2$  or  $4n+3$  (where “ $n$ ” is a whole number). In the case of nitrogen,  $A=4\times 3+2$ , and in that of phosphorus,  $A=4\times 7+3$ .

Carbon and oxygen, with atomic weights of exactly  $4n$ , give no particles, and helium also (in which  $n=1$ ) has never been disintegrated by bombardment with  $\alpha$ -particles. In the formation of the helium nucleus great energy is liberated and there is loss of mass, since the 4 protons coalesce to give a mass of 4 instead of  $4\times 1.0077$ ; but in the atoms of atomic weight,  $4n+2$  and  $4n+3$ , the odd protons are probably more loosely held and may retain their mass. “If it be supposed that the nitrogen nucleus is made up of 3 helium atoms of total mass 12, and 2 hydrogen atoms, the mass of the nitrogen atom should be not 14.00 but more nearly 14.01.” In this connection it should be noted that nitrogen contains no mass-spectra isotopes (p. 4). The tracks of ionised particles may be made visible and photographed as lines of condensed water when the  $\alpha$ -particles pass through a vessel of super-saturated water-vapour (method of C. T. R. Wilson). It may be expected that a more complete record of the collisions should thus be obtained. Such photographs have been taken in an automatic form of Wilson's apparatus by a camera which exposed two standard cinematograph films at right angles.<sup>2</sup> Twenty-three thousand photographs were taken, and a few of these showed the expected effect in a very striking manner.

<sup>1</sup> Rutherford, *Trans. Chem. Soc.*, 1922, 121, 400.

<sup>2</sup> Blackett, *Proc. Roy. Soc.*, 1925, A107, 349.

## CHAPTER III.

### NITROGEN.

Symbol, N. Atomic Weight, 14.008 (O = 16).<sup>1</sup>

**History.**<sup>1</sup>—Although D. Rutherford is generally recognised as having discovered in 1772 that nitrogen is a constituent of the air, yet it would seem that, a century before, Hooke and Mayow<sup>2</sup> had shown that the atmosphere contains two gases, one of which supports respiration and combustion. Rutherford,<sup>3</sup> after burning carbon, sulphur, phosphorus, etc., in air to remove oxygen (dephlogisticated air), treated the remaining gas with caustic alkali, and showed that the residual gas (phlogisticated air) was incapable of maintaining life. The same result was obtained by similarly treating air which had been subjected to the respiration of animals.

Priestley (1772)<sup>4</sup> was the first to show quantitatively that one-fifth of the air disappeared when charcoal was burnt in a closed vessel, and the residual gas was shaken with milk of lime. A similar result was obtained by Lavoisier (1776)<sup>5</sup> by the combustion of phosphorus, and it was Lavoisier who definitely recognised nitrogen as a simple gas, which he called *azote*—identical with the *foul air* already recognised by Scheele<sup>6</sup> as one of two gases of the atmosphere. The present name of nitrogen was suggested by Chaptal in 1823 because the gas is a constituent of nitre (Greek *nitron*).

**Occurrence.**—In the free state nitrogen occurs in the atmosphere to the extent of about 78 per cent. by volume or 75.5 per cent. by weight.<sup>7</sup> Free nitrogen is also present in volcanic gases, meteorites, and cavities of plants. In combination, nitrogen is largely distributed throughout the animal and vegetable kingdoms in the form of albuminoids, proteins, and their degradation products. In the mineral world large deposits of sodium and potassium nitrates are found in Chili and India, and it is possible that even these salts are of organic origin.

**Nitrogen Cycle in Nature.**—In nature there exists a continuous cycle whereby nitrogen is first “fixed,” and then subsequently liberated from combination with other elements. This natural cycle of operations may be conveniently represented by the diagram on p. 22.

Thus it would appear that elemental nitrogen becomes fixed from the atmosphere in two ways. Firstly, direct combination of nitrogen and oxygen occurs by means of atmospheric electricity resulting in the

<sup>1</sup> For the history of the compounds of nitrogen, see under each section.

<sup>2</sup> See *Alembic Club Reprints*, No. xvii.

<sup>3</sup> Rutherford, *De Aere Mephitico*, Edinburgh, 1772.

<sup>4</sup> See *Alembic Club Reprints*, No. vii.

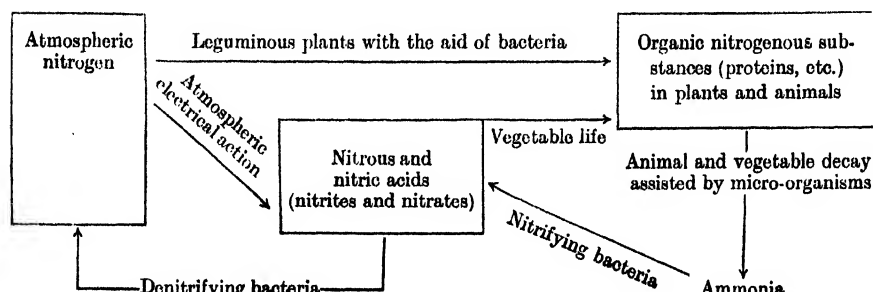
<sup>5</sup> Lavoisier, *Œuvres*, II., 99.

<sup>6</sup> See *Alembic Club Reprints*, No. viii.

<sup>7</sup> For the history and exact composition of air, see this series, Vol. VII., Part I.



production of oxides of nitrogen. These are dissolved and washed down by rain in the form of nitrous and nitric acids, which are converted into the corresponding salts by neutralisation with bases in the soil. Secondly, direct assimilation of free nitrogen takes place by leguminous plants (peas, beans, clover, etc.) with the help of bacteria. This method of nitrogen fixation is nature's compensation for the loss of combined nitrogen in the soil—the leak, as it were, being due to denitrifying bacteria. Elementary nitrogen is fixed by a large variety of azo-bacteria, which work in either a symbiotic or non-symbiotic manner, the former being the chief method. It has been known for many centuries that legumes have a very beneficial effect in restoring the fertility of the soil, but it was not until 1886 that proof was forthcoming of the presence of definite bacteria in the nodules on the roots of leguminous plants.<sup>1</sup> The isolation of *B. radicicola* followed, and its symbiotic relation to the plant itself was established by recognising that nitrogen was given to



the plant in return for carbohydrates and mineral salts from the plant to the bacterium. Non-symbiotic fixation means that bacteria work independently and not in association with other bacteria or higher plants. The bacteria are either of the anaerobic or aerobic type, and it has been generally considered that, although the anaerobic are more common and important, yet azotobacter and other aerobic nitrogen fixers have an important function. It has been recently suggested that the use of aerobic bacteria is overestimated, as the anaerobic type are capable of fixing twice the amount of nitrogen under similar conditions.<sup>2</sup>

Most plants (excepting legumes) require the nitrogen to be in some form of combination—most generally as nitrates. Broadly speaking, it is possible to trace two ways in which nitrogen is brought into a suitable condition for assimilation. In the first place, the death and decay of vegetable matter causes the complex nitrogenous substances (albumens, proteins) which have been produced during plant life to yield ultimately simple substances such as ammonia, nitrites, and nitrates. Secondly, the assimilation of vegetable products by animals results in their decomposition by metabolic processes, which produce urea, uric acid, and other faecal products. These are further broken down into simpler derivatives (ammonia, nitrates), which are now available again for plant assimilation, and the cycle starts afresh. As practically all the chemical changes are brought about directly by micro-organisms, a

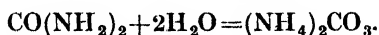
<sup>1</sup> Hellriegel and Wilfarth, *Annales Agronomiques publiées sous les auspices du Ministère de l'Agriculture et du Commerce, Paris, 1888, 5.*

<sup>2</sup> Truffaut and Bezssonoff, *Compt. rend., 1925, 181, 165.*

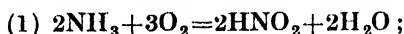
very brief account of these natural processes of ammonification and nitrification will be given.

Ammonification is the production of ammonia from proteins and their cleavage products by means of micro-organisms. Both fungi and bacteria cause extensive decomposition of albumens and proteins, first producing albumoses and peptones, then amino-acids, which are readily converted into ammonia. Amongst soil bacteria, one of the commonest is *B. mycoides*, which is very efficient in producing ammonia from organic nitrogenous materials. Energy relations are an important factor in the rapidity of decomposition of proteins. Thus both carbohydrates and proteins are utilised as sources of energy. The presence of much carbohydrate material will result in a relatively small amount of decomposition of proteins—just sufficient to provide the necessary nitrogen. In the absence of carbohydrates, proteins are quickly broken down in order to obtain a supply of carbon primarily, and the excess of nitrogen is converted into ammonia.

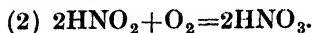
With reference to the products of animal metabolism, of which urea is typical, mention should be made of the enzyme urease which converts urea by hydrolysis into ammonium carbonate,



Nitrification is the production of nitrates, either from ammonia or nitrites, by processes of oxidation. The experiments of Schloesing and Müntz<sup>1</sup> in 1877 showed that ammonia was oxidised to nitrate by passing through a long tube filled with soil. No oxidation occurred if the soil was first sterilised, which showed that the chemical change was brought about by micro-organisms. Winogradski<sup>2</sup> in 1890 identified and isolated specific bacteria which produced this nitrification, and showed that the oxidation proceeded in two stages, each of which was brought about by different species. Thus the first oxidation of ammonia to nitrite was the work of nitrous bacteria :



while the second stage, resulting in the formation of nitrate, was caused by nitric bacteria (nitro-bacter) :



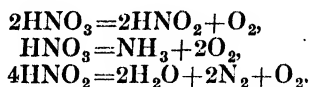
It would seem that nitrification depends upon a large number of factors, such as supply of oxygen, water, basic materials, mineral matter, etc. The importance of the amount and distribution of basic materials is due to the neutralisation of organic and mineral acids produced by bacteria, as, generally speaking, favourable conditions for both ammonifying and nitrifying organisms are only maintained if the soil is neutral or very slightly acid.

It has been mentioned that a certain loss of combined nitrogen in the soil occurs due to denitrifying organisms. Denitrification is the conversion of nitrates into nitrogen or oxides of nitrogen, and the bacteria bringing about these changes are chiefly of the aerobic type.

<sup>1</sup> Schloesing and Müntz, *Compt. rend.*, 1877, 84, 301 ; 85, 1018 ; 1878, 86, 892 ; 1879, 89, 891, 1074.

<sup>2</sup> Winogradski, *Annales Agronomiques publiées sous les auspices du Ministère de l'Agriculture et du Commerce, Paris*, 1890, 16, 273 ; *Compt. rend.*, 1891, 113, 89.

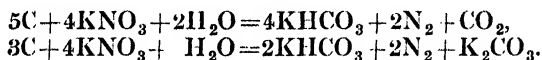
Hence insufficient aeration of the soil will force these organisms to obtain their necessary oxygen from nitrates, with the resultant loss of nitrogen. Various kinds of bacteria are able to bring about the changes represented by the following equations :—



The mutual reaction of nitrites and ammonia or amino-derivatives will also occur :



and van Iterson<sup>1</sup> has suggested that certain bacteria are capable of causing the oxidation of carbon compounds :



The prevention of denitrification is of paramount importance in market gardens and greenhouses, but appears to be of little account in field cultivation.

There are certain micro-organisms which are capable of reversing the ammonifying and nitrifying processes in order to utilise available nitrogen compounds for synthesising complex protein substances, which result in the withdrawal of nitrogen compounds for plant uses.<sup>2</sup>

#### PREPARATION OF NITROGEN.

As nitrogen is present in such large quantity in the atmosphere (more than 4000 billion tons), it is not surprising to find that at the present day a large proportion of the nitrogen used in manufactures is produced by the fractional evaporation of liquid air. A number of other methods have been utilised for obtaining nitrogen from air, and it will be obvious that these methods will all produce "atmospheric nitrogen," different from pure nitrogen in that it contains small amounts of argon and the other inert gases. Thus there are two main sources of nitrogen :

1. The atmosphere.
2. Chemical compounds.

1. The methods for obtaining nitrogen from the atmosphere may be physical or chemical.

##### (a) Physical Processes :

(1) *Liquefaction*.—The first liquefaction of air by Linde in 1889 was followed by other processes by Hampson, Pictet, and Claude. In England a combination of these systems is used by which nitrogen of 99.5 per cent. purity is obtained.<sup>3</sup>

(2) *Absorption in Charcoal*.—The greater absorption of oxygen by

<sup>1</sup> van Iterson, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 685.

<sup>2</sup> For a detailed account of the organisms in the soil, see Marshall, *Microbiology* (Churchill).

<sup>3</sup> For the liquefaction of air and the separation of nitrogen from oxygen, see this series, Vol. VII., Part I.

coconut charcoal at low temperatures allows of a partial separation of nitrogen.<sup>1</sup>

(3) *Transfusion*.—Different rates of diffusion of oxygen and nitrogen through caoutchouc gives a rough separation of these gases.<sup>2</sup>

(b) **Chemical Processes :**

The absorption of oxygen by chemical means offers a large variety of methods for preparing nitrogen.

(1) *Alkaline Pyrogallol*.—Air shaken with excess of alkaline pyrogallol has its oxygen rapidly and completely absorbed, and this experiment may be used to demonstrate the composition of air by volume.

(2) *Phosphorus*.—The formation of phosphorus oxides by passing air over smouldering or burning phosphorus results in a complete removal of oxygen. Lavoisier made use of this reaction to prove that nitrogen is a separate entity.

(3) *Copper*.—The absorption of atmospheric oxygen by passing air over heated copper, either as turnings<sup>3</sup> or finely divided metal,<sup>4</sup> can be utilised for the isolation of nitrogen. Water-vapour and carbon dioxide are previously removed by means of concentrated sulphuric acid and caustic potash. A number of methods have been devised for the absorption of oxygen at ordinary temperatures by using copper in conjunction with a mixture of air and ammonia. Lupton<sup>5</sup> proposed using ammonia gas, while Berthelot<sup>6</sup> used aqueous ammonia. A modification of this latter method consists in passing a mixture of air and "ammonia liquid" in equal volumes over copper chips. The so-called ammonia liquid is a saturated ammonium-carbonate solution mixed with an equal volume of aqueous ammonia of sp. gr. 0.93. The air-liquid mixture is completely deoxygenated after passing over the copper chips, and the residual nitrogen is freed from excess of ammonia by dilute sulphuric acid and then dried.<sup>7</sup>

(4) *Other Processes*.—Reference should also be made to some of the numerous other methods which have been proposed for the preparation of nitrogen by absorption of oxygen from air.

- (i) Reduced iron.<sup>8</sup>
- (ii) Platinum sponge<sup>9</sup> (air mixed with hydrogen).
- (iii) Sulphur burnt in a special furnace.<sup>10</sup>
- (iv) Carbonaceous matter, such as coal or petroleum.<sup>11</sup>
- (v) Fused alkali cyanides.<sup>12</sup>
- (vi) Mixture of alkali plumbate and manganate (alternate air and steam).<sup>13</sup>
- (vii) Coke-oven gases.

As air is usually a constituent of the gases derived from combustion, coke-oven distillation, etc., a number of

<sup>1</sup> See Vol. VII., Part I.

<sup>2</sup> For references, see this series, Vol. VII., Part I.

<sup>3</sup> Dumas and Bousingault, *Compt. rend.*, 1841, 12, 1005.

<sup>4</sup> Cyanide Gesellschaft, *German Patent*, 218671 (1908).

<sup>5</sup> Lupton, *Chem. News*, 1876, 33, 90.

<sup>6</sup> Berthelot, *Bull. Soc. chim.*, 1870, [iii], 13, 314.

<sup>7</sup> Brunt, *J. Amer. Chem. Soc.*, 1914, 36, 1448.

<sup>8</sup> Spencer, *English Patent*, 3752 (1869).

<sup>9</sup> Dumoulin, *Jahresber*, 1851, 32.

<sup>10</sup> Blagburn, *English Patent*, 25535 (1908); *U.S. Patent*, 993017 (1911).

<sup>11</sup> Harford, *French Patent*, 394557 (1908).

<sup>12</sup> Heys, *English Patent*, 24413 (1910).

<sup>13</sup> Kassner, *German Patent*, 233383 (1910); *Arch. Pharm.*, 1913, 25, 596; also this series, Vol. VII., Part I.

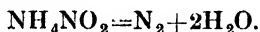
patents have been taken out for the preparation of nitrogen from these gases. A mixture of copper and copper oxide is generally used, the former to remove oxygen, and the latter to convert any carbon monoxide into carbon dioxide, and also to remove any traces of hydrogen.<sup>1</sup> Some of the processes involve the addition of small quantities of reducing gases to prevent complete oxidation of the copper, and thus save the extra cost of subsequent reduction of copper oxide. The nitrogen is freed from carbon dioxide by absorption of the latter in caustic soda.

(viii) Hydrogen.

The burning of electrolytic hydrogen is the principle of the Casale process<sup>2</sup> for removing atmospheric oxygen, and the nitrogen, after purification, is used for the manufacture of synthetic ammonia.

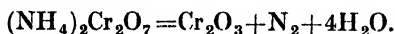
## 2. Chemical Compounds :

Ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , readily decomposes into nitrogen and water when its solution is gently heated :



Actually, in practice, it is found more convenient to warm a solution of sodium nitrite with one of ammonium chloride or sulphate, when the ammonium nitrite, formed by double decomposition, decomposes as above. Overheating should be avoided, otherwise turbulent ebullition occurs. Equal parts of sodium nitrite and ammonium sulphate dissolved in 5 parts of water and heated will give a stream of nitrogen which can be purified by passing through a dilute solution of sulphuric acid (to absorb ammonia) and then over heated copper (to remove oxides of nitrogen and oxygen). Purification can also be effected by passing the gas through a saturated solution of potassium bichromate (5 vols.) and concentrated sulphuric acid (1 vol.).<sup>3</sup>

The decomposition by heat of ammonium bichromate is a convenient method for obtaining nitrogen,



As this reaction may be rather violent, a modification is adopted by heating a mixture of potassium bichromate and ammonium chloride in a retort, when the ammonium bichromate is formed by double decomposition.

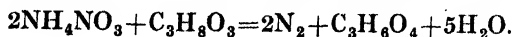
Alternatively, a concentrated solution of sodium nitrite is run slowly into a mixture of a solution saturated both with ammonium chloride and potassium dichromate. This solution is heated, and the gas evolved is washed (a) with dilute sulphuric acid, (b) with ferrous sulphate solution, and is then passed over (c) heated copper. The gas is dried by phosphorus pentoxide and then passed through a spiral cooled by liquid air. It is then frozen by liquid oxygen under reduced pressure and the solid nitrogen allowed to melt. The first fractions boiling from this are pure nitrogen, and this portion was used in the determination of physical constants by Onnes and v. Urk (see p. 81).

<sup>1</sup> Elworthy, *English Patent*, 10581 (1906); Candia and Merlini, *French Patent*, 387784 (1908).

<sup>2</sup> See p. 213.

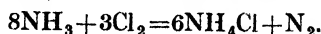
<sup>3</sup> Knorre, *Chem. Ind.*, 1902, 25, 531.

Decomposition of ammonium nitrate occurs when it is heated with glycerol, giving an almost quantitative yield of nitrogen. It would seem that nitrous oxide (from the ammonium nitrate) is completely reduced by the glycerol, the latter being converted into glyceric acid. Thus :



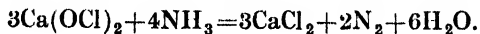
In the laboratory 10 grams of ammonium nitrate are dissolved in 20 grams of glycerol, to which 3 drops of concentrated sulphuric acid have been added. Nitrogen begins to come off at  $100^\circ\text{C}$ ., and at  $165^\circ\text{C}$ . a steady stream is obtained. It is not advisable to raise the temperature above  $170^\circ\text{C}$ . Traces of carbon dioxide are removed by passing through alkali, and moisture and minute amounts of pyridine bases by concentrated sulphuric acid.<sup>1</sup>

Pure nitrogen may be obtained by the action of chlorine gas upon ammonia :

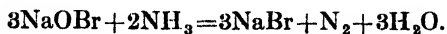


A concentrated ammonia solution (sp. gr. 0.88) is placed in a triple-necked Woulfe's bottle and chlorine is led in from a separate generator. An open glass tube passes down into the liquid through the centre neck, and a delivery tube from the third tubulure carries off the nitrogen which may be collected over water. Ammonia must always be kept in excess in order to prevent the formation of explosive nitrogen trichloride,  $\text{NCl}_3$ .

A convenient laboratory method for preparing nitrogen consists in the decomposition of concentrated ammonia solution with a thin paste of bleaching powder, which latter is added slowly. On warming the mixture a copious supply of nitrogen is obtained, in accordance with the equation



Hypobromites (bromine and caustic soda) may be used similarly to decompose ammonia :<sup>2</sup>



Hypobromites and urea (or other acid amides) react to give a mixture of nitrogen and carbon dioxide :



This quantitative reaction is used as a standard method for the estimation of urea.

Pure nitrogen is obtained when a mixture of nitric oxide (or nitrous oxide) and ammonia is passed over heated copper gauze or platinised asbestos.<sup>3</sup> The nitric oxide (from nitric acid and copper turnings) is passed through strong ammonia solution, and the mixed gases led through a heated combustion tube containing either rolls of copper gauze or platinised asbestos. Purification is effected by passing the gas successively through dilute sulphuric acid, fused caustic potash, concentrated sulphuric acid, and finally red-hot copper gauze.

<sup>1</sup> Mai, *Ber.*, 1901, 34, 3805.

<sup>2</sup> Baly and Donnan, *Trans. Chem. Soc.*, 1902, 81, 908.

<sup>3</sup> Baxter and Hickly, *J. Amer. Chem. Soc.*, 1905, 33, 300.

## THE PHYSICAL PROPERTIES OF NITROGEN.

**General.**—Nitrogen is a colourless, odourless, and tasteless gas which is non-poisonous, but does not support life. It neither burns in the ordinary way nor supports the combustion of carbon compounds. It is not inert, however, like argon, and when once in a state of chemical combination is extremely active.

**Density.**—Prior to 1898 the determinations of the weight of 1 litre of the gas under standard conditions gave values varying between 0.9713 and 0.9729, when the weight of 1 litre of air was taken as unity. These values, however, referred to atmospheric nitrogen, which of course contained the inert gases of Group O, and Rayleigh's<sup>1</sup> later determinations resulted in the value 0.97209 (air=1). For nitrogen obtained by chemical processes Rayleigh found the value of 0.96737, the weight of 1 litre being 1.25092 grams at N.T.P., while the corresponding results of Leduc<sup>2</sup> are 0.9671 (air=1) and 1.2507 gram respectively.

More recently, Moles,<sup>3</sup> as the weighted mean of a large number of determinations, calculates the weight of 1 litre of nitrogen at N.T.P. (latitude 45°) as  $1.2507 \pm 0.0001$  gram.

With reference to oxygen (=16.000), the density of nitrogen is 14.008, and to water at 4° C. the density is 0.0012507.

**Compressibility.**—The deviation of nitrogen from Boyle's law at various temperatures is seen from the subjoined table. Under relatively low pressures the molecular-attraction effect causes the gas to be more compressible, with the result that the product  $pv$  decreases in value. As is the case with most other gases, however, the molecular-volume effect soon shows its influence, and the value of  $pv$  increases with the pressure; the gas is less compressible on account of the fact that the molecules now occupy an appreciable fraction of the total volume (see table, p. 29).

The graphical relationship between  $p$  and  $pv$  shows how, at 0° C., the latter diminishes at first with rise of pressure, and, after reaching a minimum, increases again throughout with rise of pressure. As is usual, the isotherms at higher temperatures show a progressive shift of the minimum towards the region of lower pressures, and finally the minimum disappears (see fig. 6).

The limiting value of  $pv$  for nitrogen at zero pressure and 0° C., and the **molecular weight** from the ideal densities under these conditions, may be calculated as follows:—

The value of  $pv$  for nitrogen increases with decrease of pressure from 1 atmosphere to zero, which also occurs with most other gases, with the exception of hydrogen.

The coefficient  $\alpha = \frac{1}{pv} \cdot \frac{d(pv)}{dp} = -0.00056$  for nitrogen.

The corresponding value for oxygen is  $-0.00094$ , and by using Rayleigh's values<sup>4</sup> for the densities under normal conditions, the molec-

<sup>1</sup> Rayleigh, *Proc. Roy. Soc.*, 1898, 62, 209.

<sup>2</sup> Leduc, *Compt. rend.*, 1898, 126, 413.

<sup>3</sup> Moles, *J. Chim. Phys.*, 1922, 19, 283; 1924, 21, 10. See also the results of physical determinations of atomic weights, p. 57.

<sup>4</sup> Rayleigh, *Phil. Trans.*, 1905, 204, 351.

ular weight of nitrogen is given by  $32 \times \frac{0.96737}{1.10535} \times \frac{1 - 0.00056}{1 - 0.00094} = 28.016$ , where 32 = molecular weight of oxygen.

The corresponding value calculated by D. Berthelot <sup>1</sup> from the results of Leduc and Sacerdote <sup>2</sup> is 28.013.

## RELATION BETWEEN PRESSURE AND VOLUME OF NITROGEN.

(Amagat, 1893.) <sup>3</sup>

Pressure in Atm.	$pv$ at 0° C.	$pv$ at 16.03° C.	$pv$ at 99.45° C.	$pv$ at 199.5° C.
1	1.0000	..	..	..
100	0.9910	1.0620	..	..
200	1.0390	1.1145	1.4890	1.9065
300	1.1360	1.2105	1.5905	2.0145
400	1.2570	1.3290	1.7060	2.1325
500	1.3900	1.4590	1.8275	2.2570
600	1.5260	1.5945	1.9545	2.3840
700	1.6615	1.7290	2.0865	2.5125
800	1.7980	1.8655	2.2200	2.6400
900	1.9340	2.0015	2.3540	2.7715
1000	2.0685	2.1360 <sup>4</sup>	..	..
1500	2.7202	..	..	..
2000	3.3270	3.3980 <sup>4</sup>	..	..
2500	3.9200	..	..	..
3000	4.4970	4.5675 <sup>4</sup>	..	..

**Variations of  $pv$  and  $p$  with Temperature.**—The variations of  $pv$  with  $p$  at one temperature and the variations of the function  $\frac{pv}{T}$  at different temperatures have been investigated recently in the Leiden Laboratory and critically compared with the results of other workers. <sup>5</sup>

The results are best expressed in terms of a power series in which  $v^{-1}$ ,  $v^{-2}$  are multiplied by coefficients A, B, etc., derived from the experimental results. Graphically the  $pv$  values may be plotted against the densities. If the unit of volume is that at 0° C. under 1 atmosphere, and  $(pv)_0$  the value of their product under these normal conditions, the deviations with change of volume are as follows :—

At  $t=0^\circ$  C.—

$$(pv) = (pv)_0 = 1.0041 \left( 1 - \frac{0.40996 \times 10^{-3}}{v} + \frac{2.06556 \times 10^{-6}}{v^2} \right);$$

Onnes and v. Urk. <sup>5</sup>

$$(pv) = (pv)_0 = 1.0041 \left( 1 - \frac{0.43386 \times 10^{-3}}{v} + \frac{2.64643 \times 10^{-6}}{v^2} \right).$$

Holborn-Otto. <sup>6</sup>

<sup>1</sup> Berthelot, *Compt. rend.*, 1898, 126, 954.

<sup>2</sup> Leduc and Sacerdote, *ibid.*, 1897, 125, 297.

<sup>3</sup> Amagat, *Ann. Chim. Phys.*, 1893, [vi], 29, 68.

<sup>5</sup> Onnes and v. Urk, *Comm. Phys. Lab. Leiden*, No. 169.

<sup>6</sup> Holborn-Otto, *Zeitsch. Physik*, 1922, 10, 367.

<sup>4</sup> At 16.0° C.



At  $t=20^{\circ}\text{C}.$ —

$$(pv) = (pv)_0 = 1.07870 \left( 1 - \frac{0.26250 \times 10^{-3}}{v} + \frac{2.5000 \times 10^{-6}}{v^2} \right);$$

Onnes and v. Urk.<sup>1</sup>

$$(pv) = (pv)_0 = 1.07367 \left( 1 - \frac{0.27078 \times 10^{-3}}{v} + \frac{2.89454 \times 10^{-6}}{v^2} \right).$$

Holborn-Otto.<sup>2</sup>

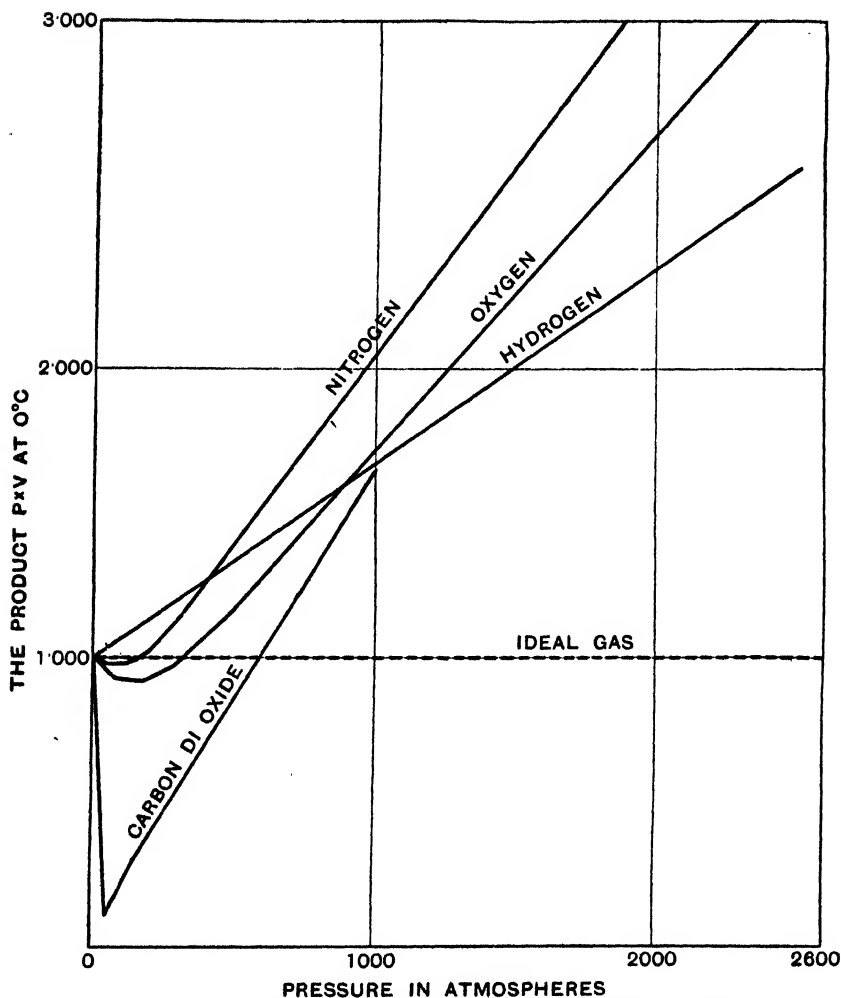


FIG. 6.—The compressibilities of oxygen and nitrogen (Amagat, 1893).

In the following table the values of  $pv$  are expressed in terms of  $(pv)_0=1$ , and the densities " $d$ " in terms of the weight of a normal

<sup>1</sup> Onnes and v. Urk, *loc. cit.*

<sup>2</sup> Holborn-Otto, *loc. cit.*

litre are given at the lowest pressures investigated at each temperature. For the full results the original memoir must be consulted.<sup>1</sup>

T. (° Abs.).	<i>p</i> (Atm.).	<i>d.</i>	<i>pv.</i>	$\frac{pv}{T}(T=t+273.09).$
298.09	35.84	33.56	1.0680	0.003644
273.09	33.14	33.52	0.9886	0.003620
250.47	33.14	37.13	0.8925	0.003578
222.83	31.98	40.83	0.7833	0.003515
191.99	30.17	46.31	0.6516	0.003394
170.84	28.54	51.185	0.5575	0.003263
151.90	26.63	56.95	0.4675	0.003077
141.72	25.29	60.675	0.4168	0.002933
131.46	23.79	65.76	0.3618	0.002750
128.63	23.20	67.15	0.3455	0.002685
126.77	22.92	68.62	0.3340	0.002634
124.51	27.93	106.06	0.2638	0.002118

The next table gives the change of *pv* with temperature at a single density of 69 (see table above) between the temperature range of 126.77° and 293.09° C.

T. (° Abs.).	<i>pv.</i>	<i>p.</i>
126.77	0.3335	23.01
128.63	0.3427	23.65
131.46	0.3566	24.61
141.72	0.4046	27.92
151.90	0.4508	31.10
170.84	0.5368	37.04
191.99	0.6303	43.49
222.83	0.7644	52.74
250.47	0.8804	60.75
273.09	0.9816	67.73
293.09	1.0670	73.62

Between  $T=81^{\circ}$  and  $85^{\circ}$  abs., and  $p=160$  and  $1326$  mm., the *pv* values are given by the equation <sup>2</sup>

$$pv=0.27774T-(0.03202-0.000253T)p.$$

The coefficient of expansion at constant pressure  $\alpha_p$ , and the coefficient of tension at constant volume  $\alpha_v$ , have been determined by a number of investigators under different pressures between  $0^{\circ}$  and  $100^{\circ}$  C. The coefficient at constant volume is numerically the same as the coefficient of tension. These two values tend to a common limit for a

<sup>1</sup> Onnes and v. Urk, *loc. cit.*

<sup>2</sup> Bestelmeyer and Valentiner, *Drude's Annalen*, 1904, 15, 60.

perfect gas when the pressure decreases indefinitely, but Regnault showed that equality of the coefficients only occurs at very low pressures.

The following table gives some typical values for these coefficients between 0° and 100° C. :—

### THERMAL EXPANSION OF GASEOUS NITROGEN.

Coefficients of Tension.			Coefficients of Expansion.		
Pressure at 0° C. in cms. of Hg.	$\alpha_p$ at 0°-100° C.	Author.	Pressure at 0° C. in cms. of Hg.	$\alpha_v$ at 0°-100° C.	Author.
100-20	0.0036744	Chappuis, <i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i> , 1903, 13, 190.	138.70 100-20	0.0036777 0.0036731	Chappuis, <i>loc. cit.</i>
79.35	0.0036718	Chappuis and Harker, <i>ibid.</i> , 1902, 12, 65.	79.20	0.0036701	Eumorfopoulos.
53.30	0.0036685		41.5	0.0036658	
52.90	0.0036681				
30.20	0.0036677				
98.50	0.0036730	Day and Clement, <i>Amer. J. Sci.</i> , 1908, 26, 405.	110.50	0.0036742	Henning and Heuse, <i>loc. cit.</i>
74.40	0.0036700		51.10	0.0036679	
55.00	0.0036680		22.0	0.0036630	
31.40	0.0036650				
110.50	0.0036752	Henning and Heuse, <i>Zeitsch. physikal. Chem.</i> , 1921, 5, 285.			
51.10	0.0036675				
22.00	0.0036626				
65.40	0.0036696				

The coefficient of expansion under limiting conditions of low density and large volume is derived from the actual coefficient under ordinary conditions, combined with a knowledge of the deviation of the actual  $p_v$  from the absolute  $(p_v)_A$  under the limiting conditions (see pp. 28 and 58, and this series, Vol. I.). Thus, if  $\alpha_A$  is this absolute coefficient, it defines the absolute temperature as given by the nitrogen thermometer,  $\left(\text{since } T_B = \frac{1}{\alpha_A}\right)$ , and the value of  $\alpha_A$  as given by the equation

$$\alpha_A = \frac{(p_v)_A \text{ at } 100^\circ - (p_v)_A \text{ at } 0^\circ}{[(p_v)_A \text{ at } 0^\circ] \times 100}.$$

The values of  $\alpha_A$  derived from the coefficients of tension,  $\alpha_p$  (see table above), are found to vary between 0.0036598 and 0.0036628, while those derived from the coefficients of expansion,  $\alpha_v$ , vary between 0.0036605 and 0.0036621.<sup>1</sup>

**Specific Heats.**—The mean specific heats of pure nitrogen at constant pressure (1 atm.) have been determined at various temperatures given in the following table.<sup>2</sup>

<sup>1</sup> Onnes and v. Urk, *Comm. Phys. Lab. Leiden*, No. 169.

<sup>2</sup> Holborn and Austin, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, p. 175; Holborn and Henning, *Ann. Physik*, 1905, 18, 739; *ibid.*, 1907, 23, 809.

$c_p$  = specific heat at constant pressure.

$C_p$  = molecular heat at constant pressure, *i.e.*  $C_p = Mc_p$ .

### SPECIFIC AND MOLAR HEATS OF GASEOUS NITROGEN AT CONSTANT PRESSURE.

$t^\circ \text{C.}$	$c_p$	$C_p$ (Molar).
0	0.2491	6.98
100	0.2501	7.01
200	0.2510	7.03
300	0.2520	7.06
400	0.2529	7.09
500	0.2539	7.11
600	0.2548	7.14
700	0.2558	7.17
800	0.2567	7.19
900	0.2577	7.22
1000	0.2586	7.25
1100	0.2596	7.27
1200	0.2605	7.30
1300	0.2615	7.33
1400	0.2624	7.35

The value of  $c_p$  is given by the equation

$$c_p = 0.2491 + 0.0000095t.$$

In the next table are given the molecular specific heats at constant volume and the ratio  $\frac{C_p}{C_v}$ .<sup>1</sup>

### MOLAR HEATS OF GASEOUS NITROGEN AT CONSTANT VOLUME, AND RATIO OF THE SPECIFIC HEATS.

$t^\circ \text{C.}$	$C_v$	$\gamma = \frac{C_p}{C_v}$
0	4.890	1.408
100	4.926	1.404
200	4.968	1.400
300	5.014	1.396
400	5.066	1.392
500	5.104	1.389
600	5.143	1.386
700	5.184	1.383
800	5.238	1.379
900	5.280	1.376
1000	5.308	1.374

<sup>1</sup> Dixon, Campbell, and Parker, *Proc. Roy. Soc.*, 1921, A100, 1.

The *thermal conductivity* of the gas at 0° C. is 0.00005660,<sup>1</sup> at 55° C. is 0.0000569,<sup>2</sup> and at 100° C. is 0.0000718.<sup>3</sup>

**Viscosity.**—The viscosity,  $\eta$ , of nitrogen is lower than that of oxygen, and therefore lower than that of air. The variations of viscosity with temperature in the case of nitrogen and air can be calculated from the formula of Sutherland :

$$\eta_T = \eta_0 \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}} \sqrt{\frac{T}{273}}$$

in which C=110 for nitrogen and 114 for air.

According to C. J. Smith,<sup>4</sup> the viscosity of air as experimentally determined at 15° C. is  $1.799 \times 10^{-4}$ , while the values for nitrogen are :

	0° C.	15° C.	100° C.
$\eta \times 10^4$	1.665	1.737	2.118

The interpolated value at 23° C. is  $1.773 \times 10^{-4}$ , while the experimental value obtained by Yen<sup>5</sup> is  $1.7665 \times 10^{-4}$ .

**Refractivity.**—The refractive index of nitrogen for sodium light is, according to Mascart, 1.0002973,<sup>6</sup> and according to Ramsay and Travers, 1.0002971.<sup>7</sup> These values refer to standard density. The constants in Cauchy's formula,

$$n-1 = A \left( 1 + \frac{B}{\lambda^2} \right),$$

are  $A=29.06$  and  $B=7.7$ , where  $n$  and  $\lambda$  represent the refractive index and wave-length respectively.<sup>8</sup>

**Spectra.**—The emission spectrum of nitrogen has been the subject of much investigation. Both the cathode and anode spectra (Geissler tube) consist of characteristic channels. Deslandres<sup>9</sup> identified three groups of lines and bands which were sharply distinguished under strong dispersion. The first group was in the visible spectrum ( $\lambda 7000-5000$ ), the second group partly in the visible and partly in the ultra-violet ( $\lambda 5000-2800$ ), and the third group wholly in the ultra-violet ( $\lambda 2800-2000$ ). Deslandres attributed the third group to an oxide of nitrogen, as this group disappeared if every trace of oxygen was removed by sodium. The second group was the most intense, and the bands at  $\lambda 3579$  and  $\lambda 3872$  were considered characteristic of nitrogen.

<sup>1</sup> Eucken, *Physikal. Zeitsch.*, 1913, 14, 324; Weber, *Ann. Physik*, 1917, [4], 54, 437.

<sup>2</sup> Todd, *Proc. Roy. Soc.*, 1910, A83, 19.

<sup>3</sup> Eucken, *Physikal. Zeitsch.*, 1911, 12, 1101.

<sup>4</sup> C. J. Smith, *Proc. Phys. Soc.*, 1922, 34, 162; Rankine and Smith, *Phil. Mag.*, 1921, [6], 42, 611.

<sup>5</sup> Yen, *ibid.*, 1919, 38, 593.

<sup>6</sup> Mascart, *Compt. rend.*, 1878, 86, 321, 1182.

<sup>7</sup> Ramsay and Travers, *Zeitsch. physikal. Chem.*, 1898, 25, 100.

<sup>8</sup> More recent values are :—

At $\lambda=6563$	5461	4861	Å.U.
$(n-1) 10^6=298.16$	299.77	301.21	

C. and M. Cuthbertson, *Proc. Roy. Soc.*, 1909, 83 [A], 152.

<sup>9</sup> Deslandres, *Compt. rend.*, 1885, 101, 1256; *ibid.*, 1886, 103, 375; *Chem. News*, 1886, 54, 100.

According to Trowbridge and Richards,<sup>1</sup> the channelled spectrum produced by a powerful continuous discharge is changed to the bright line spectrum by the introduction of a condenser. Fowler and Strutt<sup>2</sup> found that the line spectrum was characterised by a bright green line at  $\lambda 5164$ , which is followed by green bands towards the more refrangible parts of the spectrum. These two bands are between  $\lambda 4214$ — $\lambda 4199$  and  $\lambda 484$ — $\lambda 4170$ .

**Solubility.**—There are three ways of expressing the relationship of solubility by volume between gases and liquids.

(1) *Absorption coefficient*  $\beta$  (Bunsen) is the volume of gas, reduced to N.T.P., which is absorbed by unit volume of liquid, when the pressure of the gas is 760 mm. without the vapour tension of the liquid.

(2) *Solubility*  $\beta'$  is the volume of gas, reduced to N.T.P., which is absorbed by unit volume of liquid, when the total pressure is 760 mm. (i.e. including the vapour tension of the liquid),

$$\beta' = \beta \frac{760 - f}{760},$$

where  $f$  = vapour tension of liquid at the temperature of the experiment.

(3) *Solubility coefficient*  $l$  (Ostwald) is the volume of gas dissolved by unit volume of liquid at the temperature and pressure of the experiment. It is not reduced to N.T.P. Hence, if the measurements are made at atmospheric pressure,

$$l = \beta(1 + 0.00367t).$$

The following table gives the solubility of nitrogen in water in terms of the absorption coefficient  $\beta$  :—

#### SOLUBILITY OF NITROGEN IN WATER.

Temp. ° C.	Atmospheric Nitrogen.		Argon-free Nitrogen.	
	Winkler. <sup>3</sup>	Fox. <sup>4</sup>	Winkler. <sup>5</sup>	Fox.
0	0.02354	0.02359	0.02312	0.02319
10	0.01861	0.01895	0.01829	0.01863
20	0.01545	0.01598	0.01518	0.01572
30	0.01342	0.01398	0.01319	0.01375
40	0.01184	0.01252	0.01164	0.01233
50	0.01088	0.01133	0.01071	0.01160

<sup>1</sup> Trowbridge and Richards, *J. Amer. Chem. Soc.*, 1897, [4], 3, 117; *Phil. Mag.*, 1897, 43, 135.

<sup>2</sup> Fowler and Strutt, *Proc. Roy. Soc.*, 1911, A85, 371. See also Plücker and Hittorf, *Phil. Trans.*, 1865, 155, 1; Schuster, *Proc. Roy. Soc.*, 1872, 20, 485; Ångström and Thalén, *Nova Acta Soc. Upsala*, 1875, [3], 9; Hasselberg, *Mem. Acad. St Petersburg*, 1885, [7], 32, No. 15; Seguy, *Compt. rend.*, 1895, 121, 198; Sundell, *Phil. Mag.*, 1887, [5], 24, 98; Nasini and Anderlini, *Atti R. Accad. Lincei*, 1904, [5], 13, II, 59–66; Brühl, *Zeitsch. physikal. Chem.*, 1895, 16, 193, 225; *Ber.*, 1893, 26, 806, 2508; *ibid.*, 1895, 28, 2388, 2393.

<sup>3</sup> Winkler, *Ber.*, 1891, 24, 3602.

<sup>4</sup> Fox, *Trans. Faraday Soc.*, 1909, 5, 68.

<sup>5</sup> Winkler's values for atmospheric nitrogen calculated by Fox, *loc. cit.*

The formula deduced by Fox <sup>1</sup> for the solubility of pure nitrogen is

$$1000\beta = 22.998 - 0.5298t + 0.009196t^2 - 0.00006779t^3,$$

which is obtained by allowing for 1.185 per cent. argon.

*The Rate of Solution of Nitrogen in Water.*—Adeney <sup>2</sup> and his collaborators have investigated the rates of absorption of nitrogen, oxygen, and air by water under gentle agitation. Some account of this work is given in Vol. VII., p. 37. The results are summarised by the formula

$$w = (100 - w_1) \left( 1 - e^{-f \frac{A\theta}{V}} \right),$$

where

$w$  = initial percentage saturation capacity for nitrogen.

$w_1$  = amount dissolved after a given time  $\theta$ .

$e$  = Napierian logarithmic base.

$f = 0.0103 (T - 240)$ .

$A$  = area of water exposed to the gas.

$V$  = volume of water.

As in the case of oxygen, the solubility of nitrogen in sea-water decreases with increasing chlorine content. The calculated formula expressing these results is :

$$1000 \beta'' = 18.639 - 0.4304t + 0.007453t^2 - 0.0000549t^3 \\ - Cl(0.2172 - 0.007187t + 0.0000952t^2),$$

the chlorine being expressed as grams per litre.

### SOLUBILITY OF NITROGEN CONTAINING ARGON IN SEA-WATER FROM A FREE, DRY ATMOSPHERE AT 760 mm.

(Fox, 1909.) <sup>1</sup>

Parts of Chlorine per 1000.	Temperature, ° C.					
	0	4	8	12	16	20
0	18.64	17.02	15.63	14.45	13.45	12.59
4	17.74	16.27	14.98	13.88	12.94	12.15
8	16.90	15.51	14.32	13.30	12.44	11.70
12	16.03	14.75	13.66	12.72	11.93	11.25
16	15.18	14.00	13.00	12.15	11.73	10.81
20	14.31	13.27	12.34	11.57	10.92	10.36

<sup>1</sup> Fox, *Trans. Faraday Soc.*, 1909, 5, 68.

<sup>2</sup> Adeney and Becker, *Sci. Proc. Roy. Dubl. Soc.*, 1918, 15, No. 31 ; 1919, 15, No. 44 ; Adeney, Leonard, and Richardson, *Phil. Mag.*, 1923, 45, 835.

The solubility of nitrogen in aqueous solutions of sulphuric acid is given in the next table.

### SOLUBILITY OF NITROGEN IN AQUEOUS SOLUTIONS OF SULPHURIC ACID.

(Bohr.) <sup>1</sup>

Normality of Aqueous $H_2SO_4$ .	Absorption Coefficient $\beta$ at 21° C.
0	0.0156
4.9	0.0091
8.9	0.0072
10.7	0.0066
20.3	0.0049
24.8	0.0048
29.6	0.0051
34.3	0.0110
35.8	0.0129

(Christoff.) <sup>2</sup>

Per cent. $H_2SO_4$ .	Solubility Coefficient $l$ at 20° C.
0	0.015870
35.82	0.008447
61.62	0.006144
95.60	0.016720

The solubility of nitrogen in aqueous solutions of barium and sodium chlorides is as follows :—

### SOLUBILITY OF NITROGEN IN AQUEOUS SALT SOLUTIONS.

(Braun.) <sup>3</sup>

Temperature, ° C.	Coefficient of Absorption in Barium Chloride Solutions.				
	13.83 per cent.	11.92 per cent.	6.9 per cent.	3.87 per cent.	3.33 per cent.
5	0.0127	0.0137	0.0160	0.0180	0.0183
10	0.0117	0.0125	0.0147	0.0166	0.0168
15	0.0104	0.0114	0.0132	0.0148	0.0150
20	0.0092	0.0098	0.0118	0.0132	0.0135
25	0.0078	0.0086	0.0104	0.0114	0.0119
	Coefficient of Absorption in Sodium Chloride Solutions.				
	11.73 per cent.	8.14 per cent.	6.4 per cent.	2.12 per cent.	0.67 per cent.
5	0.0102	0.0127	0.0138	0.0179	0.0200
10	0.0093	0.0113	0.0126	0.0164	0.0185
15	0.0081	0.0101	0.0113	0.0147	0.0164
20	0.0066	0.0087	0.0098	0.0131	0.0148
25	0.0047	0.0075	0.0083	0.0113	0.0130

<sup>1</sup> Bohr, *Zeitsch. physikal. Chem.*, 1910, 71, 49.

<sup>2</sup> Christoff, *ibid.*, 1906, 55, 622.

<sup>3</sup> Braun, *ibid.*, 1900, 33, 721.



The following table gives the solubility of nitrogen in ethyl alcohol at various temperatures :—

### SOLUBILITY OF NITROGEN IN ALCOHOL.

(Bunsen.) <sup>1</sup>

Temperature, ° C.	0	5	10	15	20	24
Absorption coefficient	0.1263	0.1244	0.1228	0.1214	0.1204	0.1198

The solubility of nitrogen in mixtures of ethyl alcohol and water is given by Just.<sup>2</sup>

### SOLUBILITY OF NITROGEN IN AQUEOUS ETHYL ALCOHOL.<sup>2</sup>

Per cent. Alcohol.	0	20	33	99.8
Solubility product $l_{25}$	0.01634	0.01586	0.01719	0.1482

The solubility of nitrogen in natural petroleum <sup>3</sup> is of the same order as that in alcohol; the absorption coefficient at 10° C. is 0.135 and at 20° C. is 0.117.

Nitrogen is much less soluble in aqueous solutions of glycerol <sup>4</sup> and in aqueous solutions of sugars <sup>5</sup> than in water.

### LIQUID NITROGEN.

Cailletet <sup>6</sup> first liquefied nitrogen by compressing it to 200 atmospheres and allowing it to expand rapidly. Liquid nitrogen is colourless, with a refractive index of 1.2053.<sup>7</sup>

The critical data of nitrogen, according to different investigators, is given in the following table :—

### CRITICAL CONSTANTS OF NITROGEN.

Critical Temperature.	Critical Pressure.	Critical Density.	Authority.
—146	35.00	..	Olszewski, <i>Compt. rend.</i> , 1884, 98, 914.
—146.25	32.29	..	Wroblewski, <i>ibid.</i> , 1885, 100, 979; 1886, 102, 1010.
		0.31500	Happel, <i>Physikal. Zeitsch.</i> , 1902, 8, 204.
		0.32690	Dewar, <i>Proc. Roy. Soc.</i> , 1904, 73, 251.
—147.18	33.49	0.31096	Mathias, Crommelin, and Onnes, <i>Comm. Phys. Lab. Leiden</i> , 1914, No. 145c.
—144.7	33.65	..	Cardoso, <i>J. Chim. phys.</i> , 1915, 13, 812.

<sup>1</sup> Bunsen, *Gasometrische Methoden*, 1877, 2nd Edn., and *Abhandlung*, Engelmann (Leipzig, 1904).

<sup>2</sup> Just, *Zeitsch. physikal. Chem.*, 1901, 37, 361.

<sup>3</sup> Griewasz and Walfisz, *ibid.*, 1887, 1, 70.

<sup>4</sup> Drucker and Moles, *ibid.*, 1910, 75, 405; Muller, *ibid.*, 1912, 81, 496; von Hammel, *ibid.*, 1915, 90, 121.

<sup>5</sup> Drucker and Moles, *ibid.*, 1910, 75, 418; Hufner, *ibid.*, 1906, 57, 618.

<sup>6</sup> Cailletet, *Compt. rend.*, 1877, 85, 69.

<sup>7</sup> Dewar, *Proc. Roy. Soc.*, 1910, A83, 151.

The following table gives the variation of the boiling-point of nitrogen with the pressure :—

### VARIATION OF THE BOILING-POINT OF NITROGEN WITH THE PRESSURE.

Pressure, mm. (Cath.) <sup>1</sup>	Absolute Boiling- point.	Pressure, Atm. (Crommelin.) <sup>2</sup>	Absolute Boiling- point.
120·9	64·51	2·507	86·21
361·6	71·54	7·370	99·51
561·3	74·83	21·82	117·62
760	77·31	33·46 crit. pt.	125·96
938·6	79·18		
1591·1	84·21		

The empirical formula,<sup>3</sup> giving the vapour pressures of liquid nitrogen at any temperature between  $-208·36$  to  $-148·08^{\circ}$  C., may be written as :

$$\log p = -510·64/T + 12·381 - 0·12696T + 0·0008302T^2 - 0·0000019975T^3,$$

where  $T = t + 273·09$ .

### DENSITIES OF LIQUID NITROGEN AT VARIOUS TEMPERATURES.<sup>4</sup>

$t^{\circ}$ C.	Density of Liquid.	Density of Gas.
—148·08	0·4314	0·18620
—149·75	0·4799	0·16380
—153·65	0·5332	0·11170
—161·20	0·6071	0·06987
—173·73	0·6922	0·02962
—182·51	0·7433	0·01558
—195·09	0·8043	0·00490
—200·03	0·8265	0·00278
—205·45	0·8499	0·00136
—208·36	0·8622	0·00089

These values may be compared with those of earlier investigators <sup>5, 6, 7</sup>

<sup>1</sup> Cath, *Verslag Akad. Wetensch. Amsterdam*, 1918, 27, 553 ; *Comm. Phys. Lab. Leiden*, No. 152d.

<sup>2</sup> Crommelin, *Verslag Akad. Wetensch. Amsterdam*, 1914, 23, 874, 982 ; *Comm. Phys. Lab. Leiden*, No. 145d. For earlier values, see Fischer and Alt, *Drude's Annalen*, 1902, 9, 1148 ; Baly, *Phil. Mag.*, 1900, 49, 517.

<sup>3</sup> Mathias, Crommelin, and Onnes, *Comm. Phys. Lab. Leiden*, No. 162.

<sup>4</sup> Mathias, Onnes, and Crommelin, *ibid.*, 1914, No. 145c ; *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 17, 957 ; *Compt. rend.*, 1915, 160, 239.

<sup>5</sup> Wroblewski, *ibid.*, 1886, 102, 1010.

<sup>6</sup> Olszewski, *Wied. Annalen*, 1887, 31, 53.

<sup>7</sup> Drugman and Ramsay, *Trans. Chem. Soc.*, 1898, 77, 1228.

and with others, from which the following densities (of liquids only) have been selected :—

<i>t</i>	—210.5	—205	—200	—198.3	—195.5	—195.5	—190	—185	—184
<i>d</i>	0.8792 <sup>1</sup>	0.8537 <sup>2</sup>	0.8309 <sup>2</sup>	0.8297 <sup>3</sup>	0.8103 <sup>2</sup>	0.8042 <sup>1</sup>	0.7874 <sup>2</sup>	0.7622 <sup>2</sup>	0.7576 <sup>2</sup>

The latent heats of evaporation (in calories per gram) are given in the following table :—<sup>4</sup>

### LATENT HEATS OF EVAPORATION OF LIQUID NITROGEN.

<i>t</i> ° C. . .	—148.08	—148.61	—149.75	—153.65	—161.20	—173.73	—182.51	—195.09	—200.03	—205.45	—208.36
<i>T</i> ,° abs. .	125.01	124.48	123.34	119.44	111.89	99.36	90.58	78.00	73.06	67.64	64.73
<i>l</i> cals. per gram .	9.17	11.10	15.03	22.96	31.73	39.63	43.09	47.06	48.64	50.52	51.64

These latent heats may be represented by the formula

$$l^2 = 89.962(T_c - T) - 1.47242(T_c - T)^2 + 0.011666(T_c - T)^3.$$

The specific heat<sup>5</sup> of liquid nitrogen at —200.4° C., and also at —209° C., is 0.476.

*Surface Tension.*—This was first determined at —196° C. as 8.514 dynes per cm.,<sup>6</sup> while the variation with temperature is as follows :—<sup>7</sup>

<i>t</i> ° C. . .	—203	—193	—183
$\gamma$ dynes/cm. =	10.53	8.27	6.16

The change in the molar surface tension with the temperature is given by

$$r(V_M)^{\frac{1}{3}} = 2.002(124.29 - T),$$

in which  $V_M$  is the molar volume  $\frac{M}{D}$ .<sup>8</sup>

The temperature coefficient 2.002 is slightly below the mean value for normal liquids. The relation is rectilinear, as usual, up to a temperature a few degrees below the critical temperature (126° to 128° abs.).

### SOLID NITROGEN.

By rapid evaporation and cooling under reduced pressure, liquid nitrogen is converted into an ice-like solid,<sup>9</sup> which melts at —210.5° C. under a pressure of 86 mm.<sup>10</sup>

<sup>1</sup> Dewar, *Proc. Roy. Soc.*, 1904, 73, 251.

<sup>2</sup> Baly and Donnan, *Trans. Chem. Soc.*, 1902, 81, 912.

<sup>3</sup> Inglis and Coates, *ibid.*, 1906, 89, 886.

<sup>4</sup> Mathias, Crommelin, and Onnes, *Comm. Phys. Lab. Leiden*, No. 162.

<sup>5</sup> Eucken, *Ber. Deut. physikal. Ges.*, 1916, 18, 4; Keesom and Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 18, 1247.

<sup>6</sup> Grunmach, *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, p. 679.

<sup>7</sup> Baly and Donnan, *Trans. Chem. Soc.*, 1902, 81, 907.

<sup>8</sup> v. Urk, *Comm. Phys. Lab. Leiden*, 1925, Suppl. 50 to Nos. 169–180.

<sup>9</sup> Olazewski, *Compt. rend.*, 1885, 100, 979; Wroblewski, *ibid.*, 1886, 102, 1010.

<sup>10</sup> Fischer and Alt, *Drude's Annalen*, 1902, 9, 1148.

The density at  $-252.5^{\circ}$  C. is 1.0265, and the calculated density at  $-273^{\circ}$  C. is 1.1370.<sup>1</sup>

Nitrogen exists in two solid forms,<sup>2</sup> and the transition temperature is  $35.5^{\circ}$  abs., with a molecular heat of transformation of 53.8 cal.

The atomic heat increases steadily from 1.60 at  $T=15.27^{\circ}$  abs. to 5.16 at  $T=55.26^{\circ}$  abs.<sup>3</sup>

The variation in the atomic heat with temperature leads to the conclusion that crystallised nitrogen is diatomic.

The *dielectric constants* of the liquid, and also the solid form, have been determined.<sup>4</sup>

*Crystalline Form.*—The crystals which separate from the liquid at  $-210^{\circ}$  C. were considered to belong to the cubic system.<sup>5</sup> This opinion was not, however, confirmed by an X-ray analysis of the solid at  $-253^{\circ}$  C.<sup>6</sup> The matter was further tested by an observation of the solid in a cell with plane-parallel glass sides, by means of a polarisation microscope. The crystals were weakly doubly refracting, and therefore anisotropic at the melting-point and down to  $-253^{\circ}$  C. Nitrogen does not appear to crystallise on the regular system.<sup>7</sup>

## ACTIVE NITROGEN.

**History and Conditions of Formation.**—When the electrical discharge is passed through nitrogen at low pressures, a yellow glow is seen which persists for a short time after the gas has left the region of the discharge. Although this observation had been made some time before, it was left for Strutt in 1911<sup>8</sup> to examine thoroughly the physical properties of the afterglow and the chemical reactions of the active form, which differ widely from those of ordinary molecular nitrogen.

The production of the glow is powerfully catalysed by the presence of small quantities, about 0.1 per cent., of  $O_2$ ,  $CO$ ,  $CO_2$ ,  $H_2S$ ,  $SO_2$ ,  $Cl_2$ ,  $CH_4$ , and several other gases. Indeed there has been a considerable controversy as to whether it can be produced at all in absolutely pure nitrogen. Strutt prepared his nitrogen by passing the commercial gas over liquid sodium-potassium alloy, or over sodium at about  $300^{\circ}$  C., and observed the phenomena described. Tiede and Domecke<sup>9</sup> found that if oxygen is completely absent from the nitrogen, *i.e.* if it is derived from potassium or barium azide, there is no indication that the active form is produced. Further work in collaboration seemed to show that a catalyst, such as traces of the gases mentioned, must be present for the optimum activation, but that in certain forms of apparatus this may be induced in pure nitrogen.<sup>10</sup> It may, however, be taken as an established fact that atmospheric nitrogen freed from oxygen by combustion with an excess of phosphorus does not show the effect, nor was

<sup>1</sup> Dewar, *Proc. Roy. Soc.*, 1904, 73, 251.

<sup>2</sup> Eucken, *Ber. Deut. physikal. Ges.*, 1916, 18, 4.

<sup>3</sup> Keesom and Onnes, *Comm. Phys. Lab. Leiden*, No. 149.

<sup>4</sup> Ebert and Keesom, *ibid.*, No. 182.

<sup>5</sup> Wahl, *Proc. Roy. Soc.*, 1912, 87, [A], 371; *ibid.*, 1913, 88, [A], 61.

<sup>6</sup> Smedt and Keesom, *Comm. Phys. Lab. Leiden*, No. 178b.

<sup>7</sup> Vorländer and Keesom, *ibid.*, No. 182.

<sup>8</sup> Strutt (now Lord Rayleigh), *Proc. Roy. Soc.*, 1911, A85, 219.

<sup>9</sup> Tiede and Domecke, *Ber.*, 1913, 46, 340, 4095.

<sup>10</sup> Baker and Strutt, *ibid.*, 1914, 47, 2283.

it observed by Strutt in the case of commercial nitrogen which had been in contact with molten sodium for several hours.<sup>1</sup> In this connection it may be noted that although the glow is generally taken as the most important evidence that activation has taken place, it is not always a necessary concomitant of chemical activity.<sup>2</sup>

**Preparation.**—The following method of preparation is to a great extent quoted from the description by the original investigator,<sup>3</sup> and his diagram was used in drawing the apparatus.

Commercial compressed nitrogen, prepared by the rectification of liquid air, is stored over water in a gas-holder in which is hung a perforated metal bucket containing phosphorus. Before use, the gas is

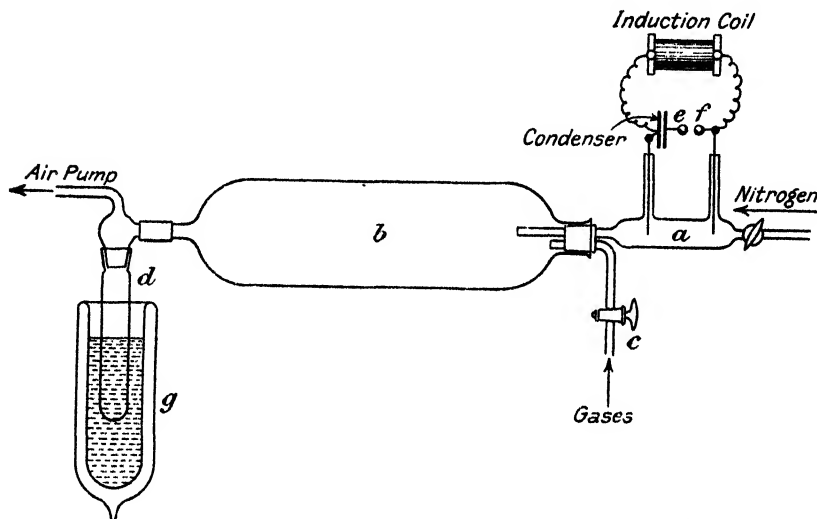


FIG. 7.—Preparation and chemical examination of active nitrogen.<sup>1</sup>

- a, discharge tube.
- b, observation and reaction tube.
- c, tube through which gases are introduced.
- d, vessel for condensation.
- e, f, spark gap.
- g, Dewar cylinder.

dried by passing through an ordinary tube of phosphorus pentoxide. A stream of this nitrogen under low pressure is passed through a tube a, in which a vigorous jar discharge is maintained.<sup>4</sup> The gas is then drawn by a powerful air-pump into the vessel b, where it exhibits a brilliant yellow light, which may persist for several minutes. The light, when analysed by the spectroscope, shows some, but not all, of the bands produced by nitrogen in a vacuum discharge. There is also a bluish-violet light which is masked by the yellow, but which may be seen by interposing a piece of blue glass. This light consists of two sets of bands, the  $\beta$  and  $\gamma$  series. The  $\beta$  bands were new, but the  $\gamma$  bands are produced when nitrous and nitric oxides are introduced into a Bunsen flame.

<sup>1</sup> Strutt, *Trans. Chem. Soc.*, 1918, 113, 200.

<sup>2</sup> Koenig and Elöd, *Ber.*, 1914, 47, 516.

<sup>3</sup> Strutt, *Proc. Roy. Soc.*, 1911, A85, 264.

<sup>4</sup> A spark gap of about six inches is required.

The yellow and blue glows may be photographed separately by using, first an isochromatic plate with a yellow screen, and then an ordinary plate with a blue screen, or no screen, since the yellow light has only a very slight effect on a photographic plate.

Some of the chemical reactions have been conspicuously demonstrated in this apparatus. When acetylene is admitted a lilac glow is developed. The hydrocyanic acid produced may be condensed by surrounding the vessel *d* with liquid air, or it may be drawn through a solution of sodium hydroxide and identified by the Prussian blue reaction. When the activated nitrogen is passed through a U-tube containing cold mercury, the surface of the mercury quickly becomes fouled, and when it is distilled with water, ammonia can be detected in the distillate by the aid of Nessler solution.

**Physical Properties of the Glow.**—The glow disappears on heating, and also under a feeble electric discharge.<sup>1</sup> At ordinary temperatures it persists for about a minute. Exposure to the temperature of liquid air intensifies it, but diminishes its duration. It is greatly increased by compression, but when the former volume is restored the capacity to produce the glow is exhausted. The heat of formation is about  $-40,000$  cal. per mol. of nitrogen<sup>2</sup> (see also pp. 44 and 46). It is not affected by an electric field, but possesses a considerable electrical conductivity, comparable to that of a salted flame.<sup>2</sup> The spectrum (see above) is not the same as that of ordinary molecular nitrogen; it contains a green, a yellow, and a red band.<sup>3</sup>

Reactions take place readily with *metals, non-metals, and compounds*. Sulphur and iodine show a blue flame. In the case of sulphur some matter, probably a sulphide of nitrogen,<sup>4</sup> is deposited on the glass.<sup>5</sup> The yellow form of this sulphide is obtained by the action of active nitrogen on sulphur chloride. White phosphorus is changed into the red variety, and at the same time a nitride is produced.<sup>4</sup> Arsenic shows a green glow and gives a nitride.<sup>4</sup>

The combination with *metals* is accompanied by beautiful and varied glows which exhibit the line spectra of the metals. The brilliant intensification of the sodium line when the metal, just above its melting-point, is brought into active nitrogen, constitutes a delicate test for the latter. Combination also occurs with zinc, cadmium, and mercury.<sup>4, 5</sup> The nitride of mercury is explosive.<sup>5</sup>

It is remarkable that neither oxygen nor hydrogen combine with active nitrogen. The extinction of the glow which is caused by ammonia or oxygen in amounts over 2 per cent., or by oxides such as those of copper or manganese, may be due to chemical action, or to a catalytic action upon the recombination of the active form.

Nitric oxide is oxidised to nitrogen trioxide, which latter may be condensed to a blue liquid in the ordinary way. The reaction probably

<sup>1</sup> According to later experiments the glow is enhanced by heating to  $225^{\circ}\text{C}.$ , destroyed by heating to  $300^{\circ}\text{C}.$ , and then only exceptionally reappears on cooling (Willey, *J. Chem. Soc.*, 1927, 2831).

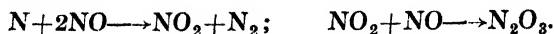
<sup>2</sup> Strutt, *Proc. Roy. Soc.*, 1911, A85, 219; *ibid.*, 1912, A87, 179.

<sup>3</sup> Strutt, *ibid.*, 1911, A85, 219; Fowler and Strutt, *ibid.*, 377; Strutt and Fowler, *ibid.*, 1911, A86, 105.

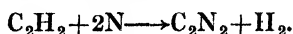
<sup>4</sup> Strutt (Lord Rayleigh), *Proc. Roy. Soc.*, 1913, 88, 539; see also *ibid.*, 1915, 91, 303; 1916, 92, 438; 1917, 93, 254.

<sup>5</sup> Strutt (Lord Rayleigh), *ibid.*, 1911, 85, 219; see also *ibid.*, 1911, 86, 56; 1912, 86, 262; 1912, 87, 180.

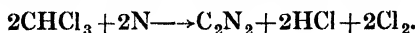
occurs in two stages. Thus, assuming that the active form consists of or liberates atoms :



Acetylene and other carbon compounds are decomposed ; the nitrogen gives cyanogen or hydrogen cyanide :



In the case of alkyl halides and chloroform, halogen is set free :



Strutt has endeavoured to determine the proportion of nitrogen converted into the active form :

(a) By absorption with phosphorus. This showed the presence of about 0.5 per cent. of the active form.

(b) By causing the gas to react with excess of nitric oxide and weighing the resulting nitrogen trioxide. This showed the presence of about 2.46 per cent. Probably this divergence is to be accounted for by the difficulty in keeping the conditions of the activation constant.

Although active nitrogen does not itself combine with oxygen (which in minute amounts favours its formation, and in larger amounts catalyses the recombination of the active nitrogen), it may yet play a part in the electrical methods of preparing oxides of nitrogen.

**Chemical Properties of another Form.**—It is well known that high-tension discharges produce both ozone and oxides of nitrogen, and are indeed necessary if a good yield of oxides is to be obtained (see Chap. XIV.). Since the same conditions lead to the formation of active nitrogen, it has been suggested<sup>1</sup> that the oxidation may be due to an interaction between active nitrogen and ozone.<sup>2</sup> In the Leatham process (1903), which was devised to prepare a bleaching gas from the air, the latter passes through an ozoniser and then through a spark gap. In an investigation of this process<sup>1</sup> it was found that passage in the reverse direction was equally effective in producing oxides of nitrogen, but that each form of discharge by itself had little effect. The amount formed was estimated by means of the absorption spectrum of  $\text{NO}_2$ , which can be detected to 1 part in 1800 by observation through a very long column (64 feet) of the gas. The active nitrogen and ozone, in insufficient amount, may be formed in the spark gap, and the further amount of ozone required in the silent discharge. The active nitrogen prepared by Strutt is not oxidised by ozone, so that it is not identical with the form prepared by Lowry.

**The Energy of Activation.**—The amount of energy evolved in the decomposition of active nitrogen with the formation of 1 molecule of molecular nitrogen,  $\text{N}_2$ , was estimated by Strutt (1911) as 1.2 to 1.8 times that evolved in the decomposition of 1 molecule of  $\text{NO}$ , i.e. 26,000 to 39,000 Cals. This result was in the main confirmed by more recent experiments, one of which will be described.<sup>3</sup> Active nitrogen, produced as described above, was mixed with nitric oxide and allowed to stream at

<sup>1</sup> Lowry, *Trans. Chem. Soc.*, 1912, 101, 1152. See also Lowry, *Phil. Mag.*, 1914, 28, 412.

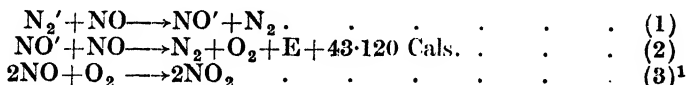
<sup>2</sup> It was already known that the combination between nitric oxide and ozone produced by electrical discharge under low pressures gave an afterglow (Strutt, *Proc. Phys. Soc.*, 1910, 23, 66).

<sup>3</sup> Willey and Rideal, *J. Chem. Soc.*, 1926, p. 1804.

a steady rate through a tube surrounded by toluene, used as the calorimetric liquid, in a Dewar flask. The temperature rose, and then attained a constant value. The same constant temperature was then attained by an electrically heated coil immersed in the same calorimeter; the electrical energy supplied per second was equal to the heat evolved per second by the reaction. It was proved by a separate experiment that this heat was evolved by that reaction which is expressed as equation (2) below, since only a small proportion of  $\text{NO}_2$  was formed in the rapid passage (0.7 sec.) of the gases through the calorimeter. The amount of  $\text{NO}_2$  produced by the subsequent oxidation at liquid air temperatures (equation 3) was determined by titrating the iodine liberated from a solution of potassium iodide. Every molecule of  $\text{NO}_2$  found, corresponds, of course, to the amounts expressed by equation (2), and since the heat of decomposition of  $2\text{NO}$  is 43,120 cals., the heat of activation  $E$  is given by the equation

$$22.400 \text{ cc. of } \text{NO}_2 = 21.560 + \frac{E}{2} \text{ Cals.}$$

The amounts of heat found by this method, and by one involving the catalytic decomposition of active nitrogen in the presence of oxygen, ranged between 36.700 and 46.000 Cals.; and the mean of the mean of results obtained by each of the two methods is 41.200 Cals. The authors consider that the reaction should be expressed by the following equations, in which the dash denotes the activated or metastable molecules :—



**Speculations as to the Nature of the Active Form.**—The electrical conductivity of active nitrogen (see above) suggests that it might simply be the ionised gas; but this hypothesis is not tenable for several reasons, among which may be mentioned the fact that the removal of charged particles which have survived the discharge has no effect upon the afterglow.<sup>2</sup>

The chemical properties would suggest that it is triatomic nitrogen, analogous to ozone, but such an allotropic form would probably be condensed at liquid air temperatures, which does not occur so far as is known at present. Additional evidence against this view is the comparatively simple nature of the spectrum.

Rayleigh himself considered that it is probably atomic nitrogen, in support of which we may note the following :—

- (a) The simplicity of the spectrum.
- (b) The groups of lines in the spectrum agree with the amounts of energy required to convert nitrogen into the atomic condition, *i.e.* a total of 11.4 volt-faradays, or 263,000 cals.<sup>3, 4</sup>
- (c) The afterglow is lengthened by heating and shortened by cooling. This behaviour is unique, and suggests that the reaction is also unique.
- (d) The rate of decay of the glow follows a bimolecular law.<sup>5</sup>

Certain difficulties in the way of this hypothesis have been stated

<sup>1</sup> A small proportion may consist of atoms which set free energy equivalent to 200,000–250,000 cals. on recombination (Willey, *J. Chem. Soc.*, 1927, 2831).

<sup>2</sup> Lewis, *Astrophys. J.*, 1900, 12, 8. See also Trautz, *Zeitsch. Elektrochem.*, 1919, 25, 299.

<sup>3</sup> Birge and Sponer, *Phys. Rev.*, 1926, 28, 283. See also Birge, *Nature*, 1926, 117, 80.

<sup>4</sup> Johnson, *Nature*, 1927, 119, 9. <sup>5</sup> Angerer, *Physikal. Zeitsch.*, 1921, 22, 4, 97.



by those who maintain the opinion that active nitrogen consists of metastable molecules in an excited condition.<sup>1</sup> The heat of activation actually observed, *i.e.* about 40·000, with a maximum of 46·000 Cals., is less than that calculated for the dissociation of nitrogen into atoms, which is estimated at more than 190·000 Cals., and is probably between 300·000 and 400·000 Cals.<sup>2, 3</sup>

A discharge which is of such a nature as to give only the line spectrum of nitrogen does not produce the afterglow.<sup>4</sup>

These difficulties may be largely overcome by supposing that active nitrogen contains at least two distinct molecular species :

(1) Metastable molecules with a lower heat of formation.

(2) A much smaller proportion of atoms which combine to form high level excited molecules with a higher heat of formation (see above).

The former are responsible for the chemical activity; the latter for the glow. These two manifestations of activity are only related to one another in a complicated manner.<sup>5</sup>

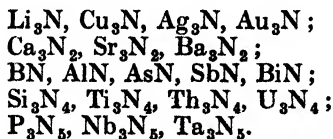
#### THE CONDITIONS OF FORMATION OF NITRIDES.

**General Considerations.**—The affinity of nitrogen for other elements is not manifested at ordinary temperatures, but on heating combination often occurs, especially in the case of the metals (and hydrogen), which combine in an exothermic manner.<sup>6</sup> The energy of combination with the more electro-positive metals (especially those of the rare earths) is considerable; thus cerium heated initially to a dull red heat in nitrogen soon becomes incandescent.

With non-metals the combination is usually endothermic, and occurs at very high temperatures; <sup>7</sup> and this is the case also with those elements which are electro-negative to nitrogen,<sup>7</sup> and which sometimes can only be caused to combine with it by indirect means.<sup>7</sup> The formulæ of the nitrides, in the cases where they have been definitely established, are usually those which are to be expected from the ordinary valency of the second element and the trivalency of nitrogen.

Nitrides can therefore be regarded as salts derived from the anhydro-acid, ammonia. In their chemical behaviour they either resemble salts of a very weak acid, being completely hydrolysed with the production of ammonia, or they are stable substances which may owe their chemical inertness to a high degree of polymerisation.

Typical formulæ are  $M_3N$ ,  $M_3N_2$ ,  $MN$ ,  $M_3N_4$ ,  $M_3N_5$ , in which the valency of the nitride-forming element *M* runs from 1 to 5; for example,



<sup>1</sup> Willey and Rideal, *J. Chem. Soc.*, 1926, p. 1804.

<sup>2</sup> Langmuir, *J. Amer. Chem. Soc.*, 1912, 34, 860.

<sup>3</sup> Eucken, *Annalen*, 1924, 440, 111.    <sup>4</sup> Fowler and Strutt, *Proc. Roy. Soc.*, 1911, 85, 377.

<sup>5</sup> Willey, *J. Chem. Soc.*, 1927, p. 2838; Kaminsky, *Zeitsch. Elektrochem.*, 1926, 32, 536.

<sup>6</sup> Thus the heat of formation of ammonia (which, strictly speaking, is hydrogen nitride,  $H_2N$ ) is +12 Cals. per mol., and that of lithium nitride,  $Li_3N$ , is +49·5.

<sup>7</sup> The heats of formation expressed in the same units are: for cyanogen,  $[C_2, N_2] = -71$  Cals.; for nitric oxide,  $[N_2, O_2] = -43·2$ ; for nitrogen trichloride,  $[N_2, 3Cl_2] = -77$  Cals.

### Survey of Methods of Preparation and Properties.<sup>1</sup>

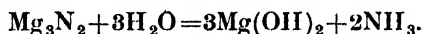
1. *Direct combination* at moderate or high temperature with the element (in the case of metals the amalgams may be used). When heated in a current of nitrogen, or when they are made the poles of an electric arc in an atmosphere of nitrogen, the following will combine :—

Li, Mg, Ca, Sr, Ba, B, Al, some metals of the rare earths, including Ce and Th, also Si, Ti, Zr, V, Nb (Cb), Ta, Cr, U, and Mn.

Lithium is one of the most reactive metals towards nitrogen ; it gives the nitride at a red heat,<sup>2,3</sup> or even in the cold.<sup>4</sup> The nitrides of the alkaline earths are formed by heating the amalgams of the metals to a dull red heat in nitrogen.<sup>5</sup>

Manganese nitride is formed in the same way from manganese amalgam. Magnesium absorbs nitrogen at a still lower temperature, as may easily be shown by a well-known experiment.<sup>6</sup> Metallic lanthanum absorbs nitrogen at 850° to 900° C. up to 9 per cent. of the weight of the metal.<sup>7</sup>

The nitrides of these reactive metals are usually dark powders which are easily hydrolysed by cold water with evolution of ammonia, *e.g.*



The reaction is in some cases so energetic that the addition of a little water raises the nitride, *e.g.* cerous nitride, to a red heat :<sup>8</sup>



The formation of nitrides by this method has been much used to separate nitrogen, as well as oxygen, from mixtures of air with the inert gases (see Vol. I., and Vol. VII., Part I.). They also supply theoretical methods of fixing nitrogen, although up to the present these methods are not commercially feasible, except perhaps in the case of AlN (see Vol. IV., and this volume, p. 217).

Chromium and manganese nitrides are not easily hydrolysed. Boron and titanium nitrides are inert powders, and are unaffected by water or aqueous acids. Silicon nitride, which is only formed at a high temperature, is also a very stable compound.

2. *The Action of Carbon and Nitrogen on Oxides.*—Aluminium nitride is formed when the oxide, mixed with carbon, is heated to a high temperature in a current of nitrogen or producer gas (nitrogen with carbon monoxide). In most cases, as in those of the oxides of the alkaline earth metals, this procedure gives, in addition, cyanide and cyanamide. Nitrides of zirconium, scandium, and niobium have also been prepared by this method.<sup>9</sup>

3. *The Action of Gaseous Ammonia on Metals or their Oxides.*—When ammonia is passed over cupric or cuprous oxide at about 300° C., a nitride, having a composition approximating to  $\text{Cu}_3\text{N}$ , can be separated from

<sup>1</sup> In accordance with the general scheme of treatment in this series, detailed accounts of the nitrides, with full references, will be found under the respective nitride-forming elements.

<sup>2</sup> Ouvrard, *Compt. rend.*, 1892, 114, 120.

<sup>3</sup> Guntz, *ibid.*, 1895, 120, 77.

<sup>4</sup> Deslandres, *ibid.*, 1895, 121, 886.

<sup>5</sup> Maquenne, *ibid.*, 1892, 114, 25.

<sup>6</sup> Merz, *Ber.*, 1891, 24, 3940; Newth, "Chemical Lecture Experiment."

<sup>7</sup> Muthmann and Kraft, *Annalen*, 1909, 325, 261.

<sup>8</sup> Muthmann and Kraft, *ibid.*, 1902, 325, 268.

<sup>9</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 293.

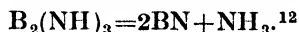
the reduced copper by dissolving the latter in a mixture of ammonia and ammonium carbonate.<sup>1, 2, 3</sup> Ammonia reacts with zinc dust at 600° C.; the product contains rather less nitrogen than is required by the formula  $\text{Zn}_3\text{N}_2$ .<sup>4</sup> Nickel and cobalt at, or slightly below, 500° C. are converted by ammonia into nitrides of variable composition.<sup>5</sup>

A nitride of iron, of inconstant composition, but corresponding approximately to  $\text{Fe}_4\text{N}_2$ , was made by passing ammonia over the finely divided metal at 460° C.<sup>6</sup> The reaction was further studied and the composition established by many researches.<sup>7, 8, 9, 10</sup> It is possible that the formation of nitrides by this method always takes place through the intermediate formation of amides and imides.

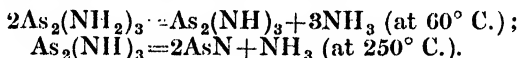
4. *The Decomposition of Amides and Imides by Heat.*—The amide of zinc yields nitride when heated to 200° C.:



Borimide (see Vol. IV.) decomposes below 130° C.:



Each of the intermediate compounds has been isolated, and the conditions of the successive changes determined in the case of arsenic:<sup>13</sup>



5. *The Action of Aqueous Ammonia.*—Aqueous ammonia at ordinary temperatures converts the oxides of silver and gold into the explosive nitrides,  $\text{Ag}_3\text{N}$ ,<sup>14</sup>  $\text{Au}_3\text{N}$ , and  $\text{Au}_3\text{N}_2$ <sup>15</sup> respectively.

6. *Reactions in Liquid Nitrogen.*—The nitrides of tin, lead, and cadmium have been prepared by passing an electric arc between electrodes of the metals immersed in liquid nitrogen.<sup>16, 17</sup>

7. *Reactions in Liquid Ammonia.*—Double decompositions which occur between halides and amides in liquid ammonia generally yield complex double amides, often with ammonia of crystallisation. But in some cases a nitride is produced, e.g. the nitride of bismuth, by the reaction between the bromide and potassium amide:



8. *The Action of Dry Ammonia on Anhydrous Chlorides (Chloranhydrides).*—This reaction is applicable more especially to the chlorides of the non-metals, and particularly those of the fifth and sixth groups.

An account of nitrogen sulphide is given on p. 203. Selenium

<sup>1</sup> Schrötter, *Annalen*, 1841, 37, 131.

<sup>2</sup> Beilby and Henderson, *J. Chem. Soc.*, 1901, 71, 1252.

<sup>3</sup> Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], 35, 201.

<sup>4</sup> White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, 28, 1343.

<sup>5</sup> Beilby and Henderson, *Trans. Chem. Soc.*, 1901, 79, 1251.

<sup>6</sup> Despretz, *Ann. Chim. Phys.*, 1829, 42, 122. <sup>7</sup> Fowler, *J. Chem. Soc.*, 1901, 79, 285.

<sup>8</sup> Beilby and Henderson, *ibid.*, 1901, 79, 1245.

<sup>9</sup> Mute and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, 28, 1343.

<sup>10</sup> Maxted, *Dissertation*, Berlin, 1911.

<sup>11</sup> Frankland, *Phil. Mag.*, 1858, [4], 15, 149.

<sup>12</sup> Moser and Eidmann, *Ber.*, 1902, 35, 535.

<sup>13</sup> Hugot, *Compt. rend.*, 1904, 139, 54.

<sup>14</sup> Raschig, *Annalen*, 1886, 233, 93.

<sup>15</sup> Raschig, *ibid.*, 1886, 235, 348.

<sup>16</sup> Fischer and Iliovici, *Ber.*, 1908, 41, 3802, 4449.

<sup>17</sup> Fischer and Schröter, *ibid.*, 1910, 43, 1400.

<sup>18</sup> Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 220.

and tellurium nitrides,  $\text{SeN}^1$  and  $\text{TeN}^2$  have also been prepared, and are described in Vol. VII., Part II. The chloronitrides of phosphorus are described in Part II. of this volume, and the nitrogen halides on pp. 114 *seq.* One preparation of boron nitride consists in leading the vapour of  $\text{BCl}_3$  with  $\text{NH}_3$  through a tube heated to  $800^\circ \text{C}$ . The product is a voluminous colourless powder, which undergoes a slight hydrolysis in the air.<sup>3</sup> Boron nitride is fully described in Vol. IV. of this series.

Zirconium nitride is prepared as a greenish-brown substance by the action of  $\text{NH}_3$  on  $\text{ZrCl}_4$ . The analysis of this product gave results corresponding most nearly to the formulæ  $\text{Zr}_2\text{N}_3$  and  $\text{Zr}_2\text{N}_8$ .<sup>4</sup>

#### ATOMIC WEIGHT OF NITROGEN.

**Historical.**—Prior to 1860, the names of Berzelius, Dulong, Gmelin, Turner, Penny, and Marignac were associated with atomic-weight determinations of nitrogen. An exhaustive series of investigations by Penny<sup>5</sup> resulted in the mean value of 13.967 from the ratio  $\text{Ag} : \text{AgNO}_3$ , and Marignac's<sup>6</sup> value for the same ratio was 13.982. This latter experimenter mentions the difficulty of obtaining pure silver nitrate, owing to the tendency of the crystals to retain nitric acid.

The elaborate researches of Stas<sup>7</sup> between the years 1860 and 1881 resulted in the mean value of 14.040 as the atomic weight for nitrogen, which was taken as standard for many years. Reinvestigation by Rayleigh, Ledue, D. Berthelot, Guye, Gray, Clarke, and others, caused a revision to be made in the atomic-weight values of a number of elements, and in 1907 the International Atomic Weight Commission adopted 14.010 as the value for nitrogen. A critical examination of the values obtained by Stas was made by Gray, who adduced considerable evidence to show that the experimental results of Stas for the atomic weight of nitrogen are erroneous. For example, the redetermination of the ratios  $\text{Ag} : \text{NH}_4\text{Cl}$  and  $\text{Ag} : \text{NH}_4\text{Br}$  by Scott,<sup>8</sup> the ratio  $\text{Ag} : \text{NaCl}$  by Richards and Wells,<sup>9</sup> and the ratio  $\text{Ag} : \text{AgNO}_3$  by Richards and Forbes,<sup>10</sup> resulted in the lowering of the Stas value in each case. Although the precautions taken by Stas were, as usual, most elaborate, yet later experimenters had many refinements not available to the great Belgian chemist. Thus, the ratio  $\text{Ag} : \text{AgNO}_3$ , according to Richards and Forbes, results in the value of 14.008 when corrections are applied for the traces of water and ammonium nitrate in the synthesised silver nitrate.

The researches on the atomic weight of nitrogen, carried out at Geneva since 1904 by P. A. Guye and his collaborators,<sup>11</sup> include the

<sup>1</sup> Strecker and Claus, *Ber.*, 1923, 56, 362.

<sup>2</sup> Metzner, *Ann. Chim. Phys.*, 1898, [7], 15, 257; *Compt. rend.*, 1897, 124, 32.

<sup>3</sup> Meyer and Zappner, *Ber.*, 1921, 54B, 360.

<sup>4</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 843.

<sup>5</sup> Penny, *Phil. Trans.*, 1833, 537.

<sup>6</sup> Marignac, *Œuvres complètes*, Geneva, 1843, 1, 87.

<sup>7</sup> Stas, *ibid.*, Bruxelles (1894).

<sup>8</sup> Scott, *Proc. Chem. Soc.*, 1900, 16, 205; *Trans. Chem. Soc.*, 1900, 77, 648; *ibid.*, 1901,

79, 147.

<sup>9</sup> Richards and Wells, *J. Amer. Chem. Soc.*, 1905, 27, 5.

<sup>10</sup> Richards and Forbes, *ibid.*, 1907, 29, 808.

<sup>11</sup> A detailed account of the physical measurements carried out in connection with this work is given by Guye in "Recherches expérimentales sur les propriétés physico-chimiques de quelques gaz en relation avec les travaux de révision du poids atomique de l'azote" (Guye, *Mém. Sci. phys. nat.*, 1908, 35, 548-694). The following account of Guye's work is reproduced from this Series, Vol. I.

analysis of nitrous oxide, both gravimetrically<sup>1</sup> and volumetrically,<sup>2</sup> the gravimetric analyses of nitrosyl chloride<sup>3</sup> and nitrogen peroxide,<sup>4</sup> the indirect volumetric analysis of ammonia,<sup>5</sup> the determination of the densities of nitrous oxide and ammonia<sup>6</sup> by the volumetric method, and the density of nitric oxide by the ordinary globe method,<sup>7</sup> and, finally, the measurement of various gaseous compressibilities<sup>8</sup> and critical constants.<sup>9</sup>

It may be stated here that all pieces of apparatus were weighed by the method of vibrations against counterpoises of similar material and shape, and of nearly equal weight, and all weighings corrected to the vacuum standard.

#### Preparation and Purification of Nitrogen Compounds Used.—

*Nitrous Oxide.*—Since the gas, prepared by any of the usual methods, is always slightly contaminated with nitrogen, recourse was had to the method devised by V. Meyer.<sup>10</sup> Concentrated sodium nitrite solution was dropped from the vessel D (fig. 10) into a neutral solution of hydroxylamine sulphate contained in the flask E. The gas evolved was passed through potassium hydroxide solution and concentrated sulphuric acid in the bottles N and P respectively, and finally dried with phosphoric anhydride in S. The solutions were prepared in air-free distilled water, and at the commencement of each experiment the apparatus was evacuated through the tube F; a small quantity of gas was then disengaged, and the apparatus again exhausted. A repetition of this procedure once or twice served to eliminate completely the last traces of air, when the tube F was sealed.

*Nitric Oxide.*—This gas was produced by three distinct methods, namely: (a) Nitric acid (25 per cent.) was allowed to flow, drop by drop, into a boiling concentrated solution of ferrous sulphate in dilute sulphuric acid, or a concentrated solution of sodium nitrite was slowly added to one of ferrous chloride in hydrochloric acid.<sup>11</sup> The evolved gas (20 litres) was collected over air-free water in a copper gas-holder, from which it was afterwards driven through concentrated sulphuric acid and over phosphoric anhydride, and the dry gas condensed in a receiver cooled in liquid air. (b) A 2 per cent. solution of sodium nitrite in concentrated sulphuric acid was run into an Erlenmeyer flask, the bottom of which was covered with a layer of mercury.<sup>12</sup> The nitric oxide produced was led through concentrated sulphuric acid, and then condensed at the temperature of liquid air. Air was initially eliminated from the apparatus by a process similar to that described under Nitrous

<sup>1</sup> Guye and Bogdan, *J. Chim. phys.*, 1905, 3, 537; *Compt. rend.*, 1904, 138, 1494.

<sup>2</sup> Jaquerod and Bogdan, *J. Chim. phys.*, 1905, 3, 562; *Compt. rend.*, 1904, 139, 94.

<sup>3</sup> Guye and Fluss, *J. Chim. phys.*, 1908, 6, 732.

<sup>4</sup> Guye and Drouguine, *ibid.*, 1910, 8, 473.

<sup>5</sup> Guye and Pintza, *Mém. Sci. phys. nat.*, 1908, 35, 594.

<sup>6</sup> Guye and Pintza, *Compt. rend.*, 1904, 139, 679; 1905, 141, 51; "Recherches expérimentales," *loc. cit.*

<sup>7</sup> Guye and Davila, *Compt. rend.*, 1905, 141, 826; "Recherches expérimentales," *loc. cit.*

<sup>8</sup> Jaquerod and Scheuer, *Compt. rend.*, 1905, 140, 1384; "Recherches expérimentales," *loc. cit.*

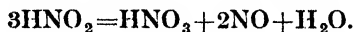
<sup>9</sup> Jaquerod, *Ber.*, 1906, 39, 1451; Briner, *J. Chim. phys.*, 1906, 4, 479; "Recherches expérimentales," *loc. cit.*

<sup>10</sup> V. Meyer, *Annalen*, 1875, 175, 141; Treadwell, *Anal. Chemie*, 1902, vol. ii. p. 512; also Treadwell-Hall, *Analytical Chemistry* (Wiley & Sons).

<sup>11</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1843, [iii], 23, 203; Thiele, *Annalen*, 1889, 253, 246.

<sup>12</sup> Emich, *Monatsh.*, 1892, 13, 73.

Oxide. (c) A 10 per cent. solution of sulphuric acid was added, drop by drop, to aqueous sodium nitrite (6 per cent.). Nitric oxide is produced in this reaction by auto-oxidation of the nitrous acid initially formed :



The gas was thoroughly dried by conducting it through three vessels containing sulphuric acid, and finally liquefied.

It will be noted that higher oxides of nitrogen were always absorbed by concentrated sulphuric acid, and not by potassium hydroxide, since the latter reagent slowly decomposes nitric oxide, producing potassium nitrite and nitrous oxide.

The impurities still present in nitric oxide, prepared by the above methods, include small quantities of nitrous oxide and nitrogen, and traces of higher oxides of nitrogen, and such substances as hydrochloric acid, sulphur dioxide, and chlorine derived from the reagents used. A consideration of the boiling-points of the impurities suggested that it should be possible to prepare nitric oxide free from all these impurities, with the possible exception of nitrogen, by liquefaction and fractional distillation. The presence of even 0.15 per cent. of nitrogen, however, would only cause an error of 0.01 per cent. in the value for the density of the gas. Accordingly, the nitric oxide was liquefied, and boiled under reduced pressure, whereby the more volatile portions escaped, and the residue solidified. It was again liquefied, the more volatile portion again boiled off, and the procedure repeated five or six times, until the volume of the liquid had been reduced by one-half. The solidified residue was then slowly sublimed, under reduced pressure, and the final third rejected. This fractional sublimation was repeated in various experiments from two to five times.

*Nitrogen Peroxide.*—This was prepared by mixing, at  $-20^\circ\text{C}.$ , purified and carefully dried nitric oxide with excess of pure oxygen, prepared from potassium chlorate. The nitrogen peroxide was repeatedly distilled under reduced pressure in the presence of oxygen, to ensure the absence of trioxide, which would have been difficult to remove by distillation. Special precautions were taken to free the final product from dissolved oxygen.

Although nitrogen peroxide decomposes into nitric oxide and oxygen at moderately high temperatures, at ordinary temperatures the extent to which this decomposition proceeds is quite insignificant, and the peroxide may therefore be regarded as a stable substance.

*Ammonia.*—Ammonia prepared from commercial ammonium salts is always contaminated with traces of organic bases such as pyridine, which materially raise its density. Accordingly, the gas obtained from a cylinder containing 20 kilograms of liquid ammonia (the first half collected in the distillation of a supply of commercial liquid ammonia) was slowly passed through a long, hard glass tube, packed with little pieces of lime and heated to redness. The organic compounds were thereby decomposed, the nitrogen contained in them being converted into ammonia. The issuing ammonia was collected in pure hydrochloric-acid solution, and on crystallisation pure ammonium chloride was obtained.

The apparatus for obtaining pure, dry ammonia for density measurements, consisted of a large cylindrical tube, filled with a mixture of pure ammonium chloride and quicklime, and connected with a purifying and

drying system of six tubes. The first three of these were filled with solid potassium hydroxide; the others contained anhydrous barium oxide. All the connections were of glass. The apparatus was initially evacuated, and then swept out once or twice with dry ammonia, liberated at a convenient rate by suitably warming the mixture of ammonium chloride and lime.

**Nitrosyl Chloride.**—This substance was prepared by Tilden's method,<sup>1</sup> a mixture of nitrosyl hydrogen sulphate and sodium chloride in equivalent quantities being warmed *in vacuo* in a small flask to 85° C. The distillate was collected in a small receiver cooled in a bath of solid carbon dioxide and ether. The materials were previously dried in a vacuum over phosphoric anhydride, and the apparatus thoroughly desiccated, since nitrosyl chloride is immediately decomposed by water. For the purification, the nitrosyl chloride was several times fractionally crystallised, the final crystals melted, and the liquid submitted to fractional distillation, with the rejection each time of the first and last fractions. The impurities thus eliminated included traces of hydrogen chloride, chlorine, sulphur dioxide, and higher oxides of nitrogen.

**Analytical Methods.**—(a) *Gravimetric Analysis.*—In the cases of nitrous oxide and nitrogen peroxide, weighed quantities of the compounds were decomposed by red-hot iron, which quantitatively absorbed the oxygen. Iron spirals were employed, wound on thin porcelain rods, and electrically heated. After an experiment, a spiral was prepared for further use by being heated in a current of pure hydrogen. Since each spiral used was oxidised and reduced a number of times in succession before the final experiments were carried out, traces of impurities in the iron, capable of forming volatile oxygen compounds, must have been eliminated.

The experimental arrangement adopted for nitrous oxide is indicated in fig. 8. The decomposition vessel A contained the iron spiral, the ends

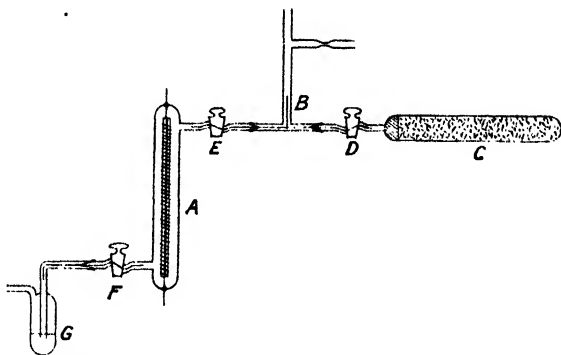


FIG. 8.—Apparatus for analysis of nitrous oxide.

of which were silver-soldered to platinum leads fused into the vessel. Connection with a mercury pump was initially made through B, which was sealed off after A had been completely evacuated. Nitrous oxide was absorbed in C, containing wood charcoal which had previously been carefully purified by igniting in chlorine, boiling with concentrated

<sup>1</sup> Tilden, *Trans. Chem. Soc.*, 1860, 12, 630, 852.

hydrochloric acid, washing with water and drying *in vacuo*. The tube C was alternately saturated with nitrous oxide and evacuated several times before being finally charged with the gas. In carrying out an analysis, A was first evacuated and weighed. The apparatus being then fitted up, B was exhausted and sealed off, the spiral heated to bright redness, and by manipulating taps D and E, nitrous oxide was passed, little by little, into A, tap F remaining closed. After the nitrous oxide in A was judged to be completely decomposed, a very slow current of the gas was allowed to pass over the incandescent spiral, the nitrogen escaping by F through the sulphuric acid in G. The current was stopped while a considerable portion of the surface of the spiral still remained unoxidised, D closed and A slowly evacuated by connecting the pump G; throughout the evacuation the spiral was maintained at a red heat to ensure the absence of any iron nitride from its surface. Finally, taps E and F were closed, and, on cooling, the increase in weight of the vessel determined. The amount of nitrous oxide used was given by the loss in weight of C.

The decomposition vessel used in the experiments with nitrogen peroxide is shown in fig. 9. It was first evacuated and weighed; pure nitrogen peroxide was distilled into it, and frozen in the tubulure A. The vessel was again exhausted, and the increase in weight, due to the peroxide, was determined. The spiral was then heated to bright redness, and the nitrogen peroxide in the tubulure allowed to evaporate slowly, its vapour being completely decomposed. The residual nitrogen was then pumped out, the spiral being still at a red heat, and finally the vacuous apparatus weighed again, after cooling, in order to determine the weight of the oxygen fixed by the iron.

For the complete analysis of nitrosyl chloride, the pure, dry vapour was very slowly led through a U-tube containing finely divided silver, heated to  $400^{\circ}$ – $500^{\circ}$  C.; special experiments showed that the chlorine was thereby quantitatively retained. The residual nitric oxide was conducted through a second U-tube containing finely divided copper at the same temperature in order to absorb the oxygen; and the nitrogen was finally absorbed by metallic calcium, contained in a straight glass tube heated to redness. Each absorption tube was provided with stop-cocks, all connections being made by ground-glass joints according to Morley's method;<sup>1</sup> and a manometer was introduced between the second and third absorption tubes. The entire apparatus was evacuated at the beginning of an experiment, and if the experiment was successful, the apparatus remained vacuous at its termination. Perfect desiccation of the interior of the apparatus was, of course, absolutely necessary; the silver and copper were prepared for use by washing with ether and drying in carbon dioxide and hydrogen respectively, while the calcium was heated to redness *in vacuo*, to eliminate any trace of volatile impurity.

(b) *Volumetric Analyses*.—A cylindrical bulb containing an iron spiral and connected by a capillary tube to a mercury manometer formed

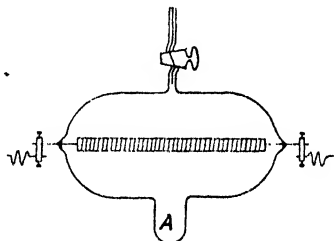


FIG. 9.—Apparatus for analysis of nitrogen peroxide.

<sup>1</sup> Morley, *Smithsonian Contrib.*, 1895, 29.



the apparatus used in the volumetric analysis of nitrous oxide. The manometer was provided with the usual opaque-glass point, to which the mercury was always adjusted whenever a measurement of pressure was required. The bulb was calibrated, and also the "dead space" along the capillary connection as far as the zero-point; and the volumes of gas were corrected for the difference in temperature between that in the bulb and the small amount in the dead space.

The bulb was initially filled with pure, dry nitrous oxide and packed with melting ice; the mercury was then adjusted to the zero-point, the pressure of the gas read (to within 0.02 mm.) and reduced to the value at 0° C. The globe was next dried and the nitrous oxide decomposed by heating the iron spiral to whiteness: to prevent permanent deformation of the bulb, the spiral was repeatedly heated to an exceedingly high temperature, but only for a few seconds at a time, the apparatus being allowed to cool considerably between successive heatings. Each experiment was continued till further heating had no influence on the final volume. Finally, the bulb was allowed to cool, packed around with melting ice, and the pressure of the residual gas observed after adjusting the mercury to zero once more.

The volumetric analysis of ammonia was indirect; the relative volumes of nitrogen and hydrogen which combine to form the gas being deduced from the densities and compressibilities of hydrogen, nitrogen, and the mixture of these gases that results from the decomposition of ammonia. The mixed gases were prepared by generating pure ammonia from ammonium chloride and quicklime, and passing it slowly through a cylindrical tube containing a platinum spiral heated to bright redness. The greater part of the ammonia decomposed; the products passed through a U-tube containing glass beads moistened with sulphuric acid to absorb unchanged ammonia, and were dried over phosphoric anhydride. The mixed gases were led into a volumeter, and the density measured as described later.

**Density Measurements.**—Modern determinations of gas densities have been effected by two methods: (i) the "globe" method, and (ii) the "volumeter" method. Each of these was employed by Guye, the former with nitric oxide, and the latter with ammonia, nitrous oxide, and the mixture of nitrogen and hydrogen obtained from ammonia.

In each method the weight of pure, dry gas, which, at an observed temperature (always 0° C. for Guye's measurements) and pressure (approximately atmospheric), occupies a known volume, is determined. The "globe" method has been already outlined (p. 130, Vol. I.); the "volumeter" method differs from it in that the measurements of pressure, volume, and temperature are effected in one apparatus, while the gas is weighed in another.<sup>1</sup>

(i) The "globe" method, first adapted to accurate work by Regnault,<sup>2</sup> is comparatively simple to carry out, permits of several experiments being conducted simultaneously, and furnishes results little, if at all, inferior to those obtained by the volumeter method. It is not necessary to employ very large globes, the results obtained with

<sup>1</sup> For the "globe" method, see Morley, *loc. cit.*; *Zeitsch. physikal. Chem.*, 1896, 20, 1; 22, 2; Rayleigh, *Proc. Roy. Soc.*, 1893, 53, 134; Leduc, *Ann. Chim. Phys.*, 1898, [viii], 15, 5; Gray, *Trans. Chem. Soc.*, 1905, 87, 1601; Perman and Davies, *Proc. Roy. Soc.*, 1906, A78, 28; Baume, *J. Chim. phys.*, 1908, 6, 1. For the volumeter method, see Morley, *loc. cit.*; Gray and Burt, *Trans. Chem. Soc.*, 1909, 95, 1633; Perman and Davies, *loc. cit.*

<sup>2</sup> Regnault, *Compt. rend.*, 1845, 20, 975.

quite small globes being at least as concordant among themselves as those obtained with 8 to 10 litre globes. Lord Rayleigh's accurate experiments were carried out with a globe the volume of which was about 1.8 litres, while the density of nitric oxide was measured by Gray, using a globe of only 0.267 litre capacity. In their work on the density of nitric oxide Guye and Davila employed three globes of capacities (at 0° C.) 379.80, 385.01, and 817.65 c.c. respectively, calibrated by weighing them empty and then filled with water at 0° C.

A small globe possesses the advantage that the correction necessary on account of its contraction when evacuated is proportionally less than that for a large globe. In fact, the only error that is augmented by employing a small globe is that due to "adsorption" of gas on the surface of the glass.

To obtain accurate results, it is absolutely necessary to have the interior of the globe perfectly dry, and to ensure this, after first repeatedly filling the globe with pure air dried by phosphoric anhydride, it is necessary to fill the globe repeatedly with the pure, dry gas and evacuate. Successive density determinations then give concordant results, provided care is taken to maintain the globe vacuous between the experiments.

The contraction undergone by each globe when evacuated was directly measured by the method suggested by Travers;<sup>1</sup> for this purpose the globe was supported in the interior of a large desiccator, its stem passing through one of the holes in a stopper in the desiccator lid. Through the other hole a calibrated vertical capillary tube was passed. The desiccator was filled with water and immersed in a constant temperature bath; the contraction of the globe was obtained by observing how far the level of the water fell in the capillary tube when the globe was evacuated.<sup>2</sup>

The globes were always filled with nitric oxide at the temperature of melting ice and under a pressure slightly in excess of atmospheric; the tap was opened to allow the pressure to fall to that of the atmosphere, and then closed again. The globe was then dried and weighed against its counterpoise.

The calculation of the results, with all necessary corrections, is explained on p. 130, Vol. I. No correction was applied for "adsorption," but allowance was made for the deviation of the gas from Boyle's Law.

(ii) The volumeter method renders it possible to deal with large quantities of gas, since the apparatus for measuring the volume need not be portable. The weight of the gas may be determined in two ways, either by disengaging the gas from an apparatus which only allows pure, dry gas to escape, and determining the loss in weight of the apparatus, or by removing the gas from the volumeter after its volume, temperature, and pressure have been determined, absorbing it by suitable means, and determining the increase in weight of the absorption apparatus and contents. The former method was used for the nitrogen-hydrogen mixture (p. 57); the latter for ammonia and nitrous oxide.

The arrangement adopted by Guye and Pintza is shown in fig. 10. The globes A and B were calibrated by determining the weight of water at 0° C. that filled them to the marks *a* and *b*. Their combined volumes

<sup>1</sup> Travers, *The Experimental Study of Gases* (Macmillan & Co., 1901), p. 119.

<sup>2</sup> Cf. Baume, *J. Chim. phys.*, 1908, 6, 16; this paper contains full details of the experimental methods used at Geneva.

amounted to 3502.63 c.c. The "dead space" extending from these marks to the tap L in one direction, and the zero-point  $n$  of the mercury manometer in the other, was separately determined, as also was the space between the taps H, I, and L.

In conducting an experiment, the absorption tube C, containing coconut charcoal, was evacuated, weighed, and attached to the apparatus as shown. The apparatus, which had previously been rinsed out several times with pure, dry gas, was evacuated, and then slowly filled with gas until the pressure was about one atmosphere. The globes were surrounded by melting ice, and when the temperature of the gas had reached  $0^{\circ}\text{C}.$ , the taps I and L were closed, the mercury adjusted to the mark  $n$ , and the initial pressure of the gas accurately observed.

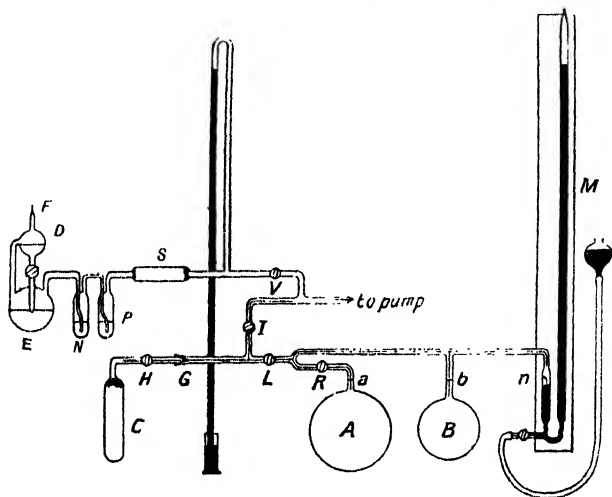


FIG. 10.—Guye's and Pintza's apparatus.

The space H I L was next evacuated, the tap I closed, and then, by suitably manipulating the taps H, L, and R, the gas was absorbed in the charcoal contained in the tube C; this tube was cooled in a bath of ether and solid carbon dioxide. After most of the gas had been absorbed, the taps H and L were closed, and the pressure of the residual gas in the globes determined. The gas contained between H, I, and L was pumped out and measured, and the absorption tube removed and reweighed.

In calculating the results, the difference between the initial and final pressures was taken, and the densities deduced according to the method given on p. 180, Vol. I.; the correction for elasticity of the glass is, however, unnecessary. Due allowance was made for the fact that the temperature of the gas in the dead space was not  $0^{\circ}\text{C}.$ , and the results were corrected for the known deviations of the gases from Boyle's Law.

Guye and Pintza considered that by still leaving an appreciable amount of gas in the volumeter at the end of an experiment, any "adsorption" effect was eliminated from their results; but this conclusion is erroneous (see p. 108, Vol. I.).

Reference only can be made to the measurements of compressibilities and critical constants (*vide supra*).

**Statement of Results.**—*Analytical Methods.*—(i) Gravimetric analysis of nitrous oxide. In five experiments,

5·6269 grams nitrous oxide yielded 2·0454 grams oxygen.

Hence

$\text{N}_2\text{O} : \text{O} :: 44·015 : 16$ , and  $\text{N}=14·008$ .

The presence of a trace of air or oxides of carbon in the gas would lead to a slightly high value for the atomic weight of nitrogen.

(ii) Gravimetric analysis of nitrogen peroxide. In seven experiments,

10·3522 grams nitrogen peroxide yielded 7·1999 grams oxygen.

Hence

$\text{NO}_2 : \text{O}_2 :: 46·010 : 32$ , and  $\text{N}=14·010$ .

A trace of oxygen dissolved in the nitrogen peroxide would cause the result to be rather low.

(iii) Gravimetric analysis of nitrosyl chloride. In five experiments,

0·6067 gram nitrogen was obtained and 0·6981 gram oxygen.

Hence

$\text{N} : \text{O} :: 14·006 : 16$ , and  $\text{N}=14·006$ .

(iv) Volumetric analysis of nitrous oxide. As the mean of four experiments,

1 litre of nitrous oxide at N.T.P. yielded 1·00717 litres of nitrogen.

But increase in volume of iron spiral, due to oxidation, amounts to 0·30 c.c. ; hence corrected volume of nitrogen is 1·00687 litres. Also

1 litre of nitrous oxide at N.T.P. weighs 1·9777 grams (*vide infra*);  
1 „ nitrogen „ „ 1·2507 „ (Rayleigh).

Hence

$(\text{N}_2\text{O}-\text{N}_2) : \text{N}_2 :: 16 : 28·042$ , and  $\text{N}=14·021$ .

(v) Volumetric analysis of ammonia. As the mean of three experiments,

Weight of “ normal ” litre of mixed hydrogen and nitrogen

=0·8799 gram.

Assuming the data of other observers for the densities and compressibilities of hydrogen and nitrogen, it follows from this result that the molecular volumes of these gases are in the ratio of 1·00057 : 1 at N.T.P., and

$\text{H}_2 : \text{N}_2 :: 2·0152 : 28·030$ , whence  $\text{N}=14·015$  ( $\text{H}=1·0076$ ).

Guye and Pintza only attach a confirmatory significance to this result, and therefore the details of the calculation are omitted.

*Physical Methods.*—(a) *Data.*—The values obtained for the weight in grams of a normal litre of gas are as follows :—

$\text{NH}_3$	.	.	.	.	0·77079	(mean of 5)
$\text{N}_2\text{O}$	.	.	.	.	1·9777	( „ 3)
$\text{NO}$	.	.	.	.	1·8402	( „ 14)

The following are the values of  $A_0^1$  at  $0^\circ$  C. (sec p. 132, Vol. I.)<sup>1</sup> :—

$\text{NH}_3$ .	$\text{N}_2\text{O}$ .	$\text{NO}$ .
+0.01521	+0.00742	+0.00117
	(Rayleigh)	

The critical constants are as follows :—

	$\text{NH}_3$ .	$\text{N}_2\text{O}$ .	$\text{NO}$ .
Critical temp. (abs.).	405.3°	311.8°	179.5°
„ press. (atm.)	109.6	77.8	71.2

The values for nitrous oxide and nitric oxide are due to Villard<sup>2</sup> and Olszewski<sup>3</sup> respectively.

(b) *Calculation of Molecular Weights; Atomic Weight of Nitrogen.*—

(i) By Limiting Densities. Assuming the values 1.4290 and +0.00097 respectively for the normal density and the coefficient  $A_0^1$  for oxygen, and applying the formula (3) deduced on p. 132, Vol. I., we have :

	L.	$1 - A_0^1$	Molecular Weight.	Atomic Weight of Nitrogen.
$\text{NH}_3$ . .	0.7708	0.98479	17.015	13.992
$\text{N}_2\text{O}$ . .	1.9777	0.99258	44.001	14.001
$\text{NO}$ . .	1.3402	0.99883	30.006	14.006
$\text{O}_2$ . .	1.4290	0.99903	32.000 (standard)	..

(ii) From Critical Constants. Applying the formulæ of p. 134, Vol. I., to the data already given, the following results are obtained :—

	L.	$10^{-5}a$ .	$10^{-5}b$ .	$10^{-5}a_0$ .	$10^{-5}b_0$ .	Molecular Weight.	Atomic Weight of Nitrogen.
$\text{NH}_3$ .	0.7708	859	170	1554	146	17.036	14.013
$\text{N}_2\text{O}$ .	1.9777	719	185	878	156	44.008	14.004
$\text{NO}$ . .	1.3402	257	115	..	..	30.009	14.009

**Summary of Results.**—The various results obtained by Guye and his collaborators for the atomic weight of nitrogen are given in the following table :—

Analytical.				Physical.			
Gravimetric Analysis.		Volumetric Analysis.		Density Limits.		Critical Constants.	
$\text{N}_2\text{O} : \text{O}$	14.008	$\text{N}_2\text{O} : \text{N}_2$	14.021	$\text{NH}_3$	13.992	$\text{NH}_3$	14.013
$\text{NO}_2 : \text{O}_2$	14.010	$\text{N} : 3\text{H}$	14.015	$\text{N}_2\text{O}$	14.001	$\text{N}_2\text{O}$	14.004
$\text{N} : \text{O}$	14.006	(indirect)		$\text{NO}$	14.006	$\text{NO}$	14.009
(in $\text{NOCl}$ )							

<sup>1</sup>  $A_0^1$  is the symbol for the second gas in Vol I. *loc. cit.*, and  $A_0^1$  for the standard gas, oxygen.

<sup>2</sup> Villard, *Compt. rend.*, 1894, 118, 1096.

<sup>3</sup> Olszewski, *Phil. Mag.*, 1895, [v], 39, 188.

The mean of the three gravimetric values is  $N=14.008$ , much the best series being undoubtedly that relating to the analysis of nitrogen peroxide; in each case the determination was a direct one.

The results of the volumetric analysis confirm the gravimetric value; the value obtained from the analysis of nitrous oxide depends, however, on the densities of nitrous oxide and nitrogen as well as on the volumetric ratio measured, while the uncertainty concerning the value deduced from the analysis of ammonia has been already mentioned.

Turning to the physical results, it is seen that the mean value deduced by the method of critical constants is  $N=14.009$ , in close agreement with the gravimetric value. It should be remembered, however, that this method of calculation is empirical, although it yields good results for a number of other atomic weights (see p. 135, Vol. I.).

The results obtained by the method of limiting densities are, in the cases of ammonia and nitrous oxide, distinctly lower than the gravimetric value. These two gases are readily liquefied, and with such gases the molecular weights obtained by this method are usually rather low, probably owing to  $A_0$  being overestimated. The method of extrapolating for  $A_0$ , adopted by Jaquero and Scheuer for ammonia, is open to criticism; while Rayleigh's value for  $A_0$  for nitrous oxide is almost certainly too large, since it is obtained by a linear extrapolation. The value  $N=14.006$  furnished by nitric oxide is, however, in good agreement with the gravimetric value, as also is the value deduced from the density and compressibility of nitrogen.<sup>1</sup>

The experimental work carried out at Geneva therefore leads to the rounded-off value  $N=14.01$ .<sup>2</sup>

A description of the work of R. W. Gray<sup>3</sup> is now given as confirming, in a remarkable manner, the values obtained by Guye. Gray preferred nitric to nitrous oxide on account of the close approximation with which the former gas obeys the gas laws at ordinary temperatures, and also because nitric oxide contains nitrogen and oxygen in approximately equal weights.

*Preparation and Purification of Nitric Oxide.*—Great precautions were taken to obtain nitric oxide free from nitrogen and nitrous oxide. The gas was prepared by Deventer's method from potassium nitrite, potassium ferrocyanide, and acetic acid. Nitrogen tetroxide was removed by means of strong aqueous caustic potash, and the gas was then passed over solid caustic potash, and finally over phosphorus pentoxide to remove water.

An extensive series of fractionations was then performed in order to remove completely nitrous oxide and nitrogen. The crude, dried nitric oxide was liquefied in a vessel surrounded by a vacuum vessel, and a fresh supply of gas bubbled through the liquid and condensed in a second vessel, which communicated with a similar third vessel, so that the gas which solidified in this last container had again passed through its own liquid in the second vessel. The nitric-oxide gas from the third vessel

<sup>1</sup> Berthelot, *Compt. rend.*, 1898, 126, 954, 1030, 1415, 1501.

<sup>2</sup> For a full discussion of the atomic weight of nitrogen, see Guye, *Bull. Soc. chim.*, 1905, 33, 1; *Chem. News*, 1905, 92, 261, 275, 285; 1906, 93, 4, 13, 23, 35; Gray, *Trans. Chem. Soc.*, 1906, 89, 1174; and for further modern work on the atomic weight of nitrogen, see Gray, *Trans. Chem. Soc.*, 1905, 87, 1601; Perman and Davies, *Proc. Roy. Soc.*, 1906, A78, 28; Richards and Forbes, *J. Amer. Chem. Soc.*, 1907, 29, 826; Richards, Koethner, and Tiede, *ibid.*, 1909, 31, 6; Wourtsel, *Compt. rend.*, 1912, 154, 115.

<sup>3</sup> Gray, *Trans. Chem. Soc.*, 1905, 87, 1601.

was now largely freed from nitrous oxide, and was stored over water in a gas-holder. After passing the gas over solid caustic potash and phosphorus pentoxide, the gas was subjected to another series of fractionations, after which it was possible to demonstrate complete absence of nitrous oxide.

The removal of the last traces of nitrogen was a matter of greater difficulty owing to the occlusion of nitrogen by the solid nitric oxide. Although most of the nitrogen could be removed by means of the Töpler pump, removal of traces was only effected by subliming the solid gas under 170 mm. pressure, at which the boiling-point and melting-point of nitric oxide coincide. Finally, the solid nitric oxide was sublimed under a pressure of 50 mm., and the last traces of nitrogen removed through the Töpler pump.

*Determination of the Density of Nitric Oxide.*—The density of nitric oxide was determined relatively to that of oxygen by filling a glass bulb of about 300 c.c. capacity with the purified gas, after first exhausting the bulb by means of the Töpler pump. The greatest precautions in weighing were taken. Thus, the sealed counterpoise bulb and that containing the gas were treated in an identical manner. The weights of nitric oxide and oxygen were then compared by filling the bulb with pure oxygen under similar conditions.

The weight of a litre of nitric oxide was found to be 1.3402 grams, when Rayleigh's figure was used for the weight of a litre of oxygen at N.T.P., lat. 45°, namely, 1.42905 grams.

The exact molecular weight of nitric oxide was calculated (a) by using the results of Jaquero and Scheuer<sup>1</sup> for the relative compressibilities of nitric oxide and oxygen, and found to be 30.004; (b) by reduction to 0° C. of the critical constants,<sup>2</sup> and found to be 30.008.

The physical value for the atomic weight of nitrogen was thus found :

(i) Method of limiting densities . . .	14.004
(ii) Reduction of critical constants . . .	14.008
Mean value . . .	14.006

*The Gravimetric Analysis of Nitric Oxide.*—For the purpose of very exact analysis, the nitric oxide was subjected to a third fractionation and sublimation. The apparatus employed is illustrated in fig. 11. Into the neck of the combustion bulb A was fitted a carefully ground glass stopper B carrying two thick (2 mm. diam.) platinum electrodes EE. Fused to the stopper were a capillary tube and a stop-cock joined to a capillary ground glass joint D. Attached to the electrodes were leads of thick nickel wire supporting a small porcelain boat H. About 75 cm. of fine platinum wire were evenly wound around the whole length of the boat and connected with the nickel leads. By this arrangement the boat and its contents could be raised to any desired temperature by passing an electric current through the electrodes EE.

By means of a short length of capillary glass tubing, the bulb A was connected with the nitrogen absorption bulb M. The latter, which was filled with powdered coconut charcoal, was connected by means of a second ground capillary joint K with the rest of the apparatus. A stop-cock D led to a tube connected on the one side with the Töpler

<sup>1</sup> Jaquero and Scheuer, *Bull. Soc. chim.*, 1905, [ii], 33-44, 44.

<sup>2</sup> Guye, *ibid.*, 1905, 33, 1.

pump and on the other with the storage bulbs containing the nitric oxide. The capacity of the bulb A was about 300 c.c., whilst that of M was about 100 c.c.

In carrying out an experiment the gas was decomposed in the combustion bulb A. The nitrogen was completely absorbed in the bulb M,

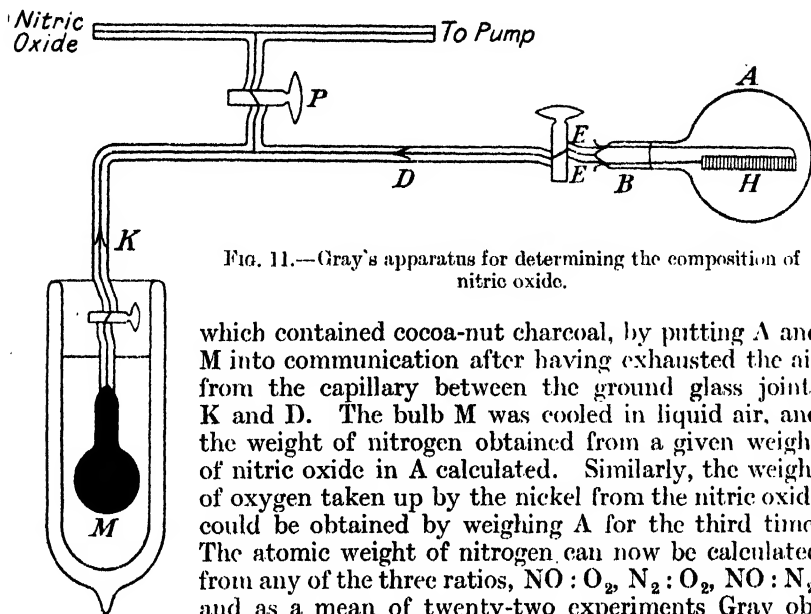


FIG. 11.—Gray's apparatus for determining the composition of nitric oxide.

which contained cocoa-nut charcoal, by putting A and M into communication after having exhausted the air from the capillary between the ground glass joints K and D. The bulb M was cooled in liquid air, and the weight of nitrogen obtained from a given weight of nitric oxide in A calculated. Similarly, the weight of oxygen taken up by the nickel from the nitric oxide could be obtained by weighing A for the third time. The atomic weight of nitrogen can now be calculated from any of the three ratios,  $\text{NO} : \text{O}_2$ ,  $\text{N}_2 : \text{O}_2$ ,  $\text{NO} : \text{N}_2$ , and as a mean of twenty-two experiments Gray obtained the value 14.010.

The density of the nitrogen resulting from the decomposition of nitric oxide was obtained by substituting a density bulb for M, and the mean of two experiments gave the value of 14.008 for the atomic weight of nitrogen.

The final conclusion of Gray, obtained by giving each individual result an equal value, is that the atomic weight of nitrogen is 14.0085, which agrees excellently with the value of 14.0090 as the result of the contemporary work of Guye and his collaborators.

Wourzel<sup>1</sup> in 1912 calculated the ratio  $\text{N}_2 : \text{O}_2$ , determined from the weight of oxygen required to convert nitric oxide into nitrogen peroxide, and obtained 14.0068 as the average atomic weight of nitrogen from five concordant results.

More recent determinations are in good agreement with the results of Guye and Gray, and the accepted value of 14.008 may be considered as correct to 2 or 3 in the fifth significant figure. Moles and Clavera<sup>2</sup> give 14.008 from the density of nitrogen prepared by ignition of pure sodium azide,  $\text{NaN}_3$ . Batuecas,<sup>3</sup> from the densities and compressibilities of nitrous and nitric oxides, obtains the values 14.003 and 14.006.

<sup>1</sup> Wourzel, *Compt. rend.*, 1912, 154, 115.

<sup>2</sup> Moles and Clavera, *J. Chim. phys.*, 1924, 21, 10.

<sup>3</sup> Batuecas, *ibid.*, 1925, 22, 101.



## CHAPTER IV.

### AMMONIA, $\text{NH}_3$ .

**History.**—The name “ammonia” is derived from “sal armoniacum” or “sal ammoniacum,” terms used to designate the carbonate and chloride, which were articles of commerce from early ages, and were obtained from organic substances containing nitrogen, *e.g.* by heating camel’s dung or, later, by heating together urine and common salt (Geber) (see this series, Vol. II., Chap. VIII.). The terms were applied in the Middle Ages with a variable significance. By the eighteenth century the word “sal ammoniac” had become fixed in its present meaning. Ammonia in solution was first prepared by the distillation of animal refuse, such as horns and bones, and hence was called “*spirit of hartshorn*.”

Ammonia gas was isolated and collected by Priestley in 1774 by heating sal ammoniac with lime and collecting over mercury. He termed the gas “alkaline air.” The absorption of the gas in water had been previously shown by Stephen Hales in 1727, and the name ammonia was given to this solution by Bergmann in 1782. Priestley demonstrated the almost complete decomposition of “alkaline air” into “inflammable air” after the passing of electric sparks, and Berthollet in 1785 showed that the residual gas consisted of nitrogen and hydrogen. The composition of ammonia was determined by Austin in 1788, Davy in 1800, and Henry in 1809. The partial synthesis of ammonia by the spark discharge was effected by Deville in 1865 and by Donkin in 1873.<sup>1</sup> It was also early shown that by long-continued sparking of a mixture of nitrogen and hydrogen over hydrochloric or sulphuric acid, a great part, and finally the whole, of the  $\text{N}_2 + 3\text{H}_2$  can be absorbed as ammonium salt.

**Occurrence.**—In small amounts ammonia is found in the air, in water, and in the earth. It is usually derived from the bacterial decomposition of animal and vegetable proteins (see p. 21, Circulation of Nitrogen): this is the source of the free ammonia and its salts, which are found in natural waters. The Stassfurt salt deposits contain ammonium salts, and the sulphate and chloride are found in some volcanic minerals. Ammonia is sometimes found in volcanic gases, and in the steam and water of hot springs; here it has probably been derived from the hydrolysis of nitrides, *e.g.* in the Tuscan soffioni from boron nitride. The mineral *struvite*,  $\text{MgNH}_4\text{PO}_4$ , is probably derived from the decay of organic matter.

**Source.**—Ammonia, together with organic bases, is produced during the destructive distillation of nitrogenous organic matter. The ammonia obtained as a by-product in the distillation of coal for gas was formerly the only abundant source of this compound and its salts, and still furnishes a considerable proportion of the world’s production.

<sup>1</sup> Donkin, *Proc. Roy. Soc.*, 1873, **21**, 281.

Coal contains about 1.0 to 1.6 per cent. of nitrogen. Of this, about one-fifth is usually recovered as ammonia. Some is evolved as nitrogen, some as cyanides, and a part, usually from 30 to 65 per cent., remains in the coke, perhaps as nitride. Between 1 and 2 per cent. passes into the tar.

The yield of ammonia from the distillation of coal is much increased by the injection of steam. The Mond process for the production of power gas increases the amount of ammonia about threefold; the weight of ammonium sulphate recovered may be about 3 per cent. of the weight of the coal gasified.<sup>1,2</sup> Ammonia may also be obtained by passing air and atomised water through peat at about  $400^\circ \text{C}$ . The gases after scrubbing must be passed through lime to absorb acetic acid, and then through sulphuric acid to form the sulphate, in which form ammonia is usually supplied as a fertiliser.

The crude ammonia liquor, obtained as a by-product in the manufacture of coal gas, contains 12 to 35 grams of  $\text{NH}_3$  per litre, partly as the free base, partly as ammonium salts, such as carbonate, bicarbonate, sulphide, thiosulphate, sulphate, chloride, cyanide, and thiocyanate. On distillation with sufficient milk of lime, the whole of these acids remain combined with the lime, and the whole of the ammonia is obtained in the distillate. The usual practice, however, is to cause the salts of the volatile and weak acids to dissociate by heat, and to fix only the non-volatile and strong acids by the addition of lime in the calculated amount, which is about one-third of that required by the first method.

The ammoniacal liquor is run into the top of a fractionating column or tower, and heated by enclosed steam coils to about  $95^\circ \text{C}$ ., at which temperature the carbonate, sulphide, etc., are largely dissociated, and the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  almost completely evolved, *i.e.* to the extent of 80 per cent. and 60 to 70 per cent. respectively. The escaping gases are washed with sulphuric acid in order to retain traces of ammonia before being passed on for treatment for the recovery of cyanogen and sulphur compounds.

The ammonia and steam may be condensed in cold water, giving a liquor with 15 to 20 per cent. of  $\text{NH}_3$ . The residual liquor from the lower part of the tower, containing ammonium sulphate, etc., falls into a vessel containing milk of lime, and the ammonia evolved is distilled in a current of steam.

The required amount of milk of lime may also be added to the original liquor, and the distillate purified by passing through a rectifying tower containing a paste of lime and ferric hydroxide.

The vapours of ammonia and steam from any of these processes are more commonly absorbed in sulphuric acid—first 20 per cent., then 60 per cent.—and on evaporation yield a good grade of ammonium sulphate.

The world's production of ammonia obtained as a by-product from coal gas and coke-oven gas is between one and two million tons. The poor yield of ammonia in coal gas or coke-oven distillation with by-product recovery can be accounted for (a) by the nitrogen which remains in the coke, and (b) by the loss of ammonia first formed. While (a) is proved to be a true cause by analysis, experimental evidence has

<sup>1</sup> Mond, *English Patent*, 12440 (1893).

<sup>2</sup> In coke-oven distillation with by-product recovery, from 76 to 90 lb. of ammonium sulphate per ton of coal can be obtained if ammonia recovery be the principal object.

also been adduced in favour of (b) as an important cause. The reactions which proceed between a porous coke, its ash, steam, and ammonia are somewhat complex. It is known that up to 9 per cent. of water added to the coal increases the yield. It may be effective in this respect by lowering the temperature, by diluting the ammonia and so decreasing its active mass, or by hydrating and so protecting the molecules. Above 9 per cent. of water decreases the yield. The catalytic decomposition of ammonia by the substances which will be present in a coke oven has been investigated by Foxwell,<sup>1</sup> and the reader is referred to his paper for a complete account. The maximum amount is formed in the coke oven at about 800° to 900° C.

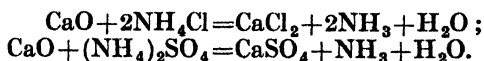
It was shown by Ramsay and Young<sup>2</sup> that ammonia is completely destroyed when passed through an iron tube packed with porcelain.

The equilibrium amounts of ammonia which can be formed from coke-oven gas of average composition may be calculated from the Haber equation, and are quite low, namely, 0.0034 per cent. at 800° C. The problem, therefore, is to destroy as little as possible of the ammonia produced by distillation at the optimum temperature. Although pure, dry ammonia begins to dissociate at 620° C., and the decomposition temperature is considerably lowered by the presence of organic matter or water,<sup>3</sup> yet since this dissociation is not instantaneous, but takes an appreciable time, sufficient undissociated ammonia will be left to give a fair yield even at the higher temperatures. The velocity constants for the decomposition in the presence of coke have been determined by Foxwell.<sup>1</sup> The reaction is found to be bimolecular, and the constant "*k*" derived from the equation

$$k = \frac{1}{t} \left( \frac{1}{a-x} - \frac{1}{a} \right)$$

is 0.00015 at 520° C., rising to 0.00215 at 755° C. and 0.0057 at 850° C. A much smaller constant is obtained with ammonia which is in contact with silica brick alone, but a larger one if the brick is high in iron, some samples giving a constant about six times that found in the presence of coke (at 755° C.). Iron, originally present as oxide, powerfully catalyses the decomposition, as it does also the formation of ammonia (see p. 103); but iron added in the form of pyrites has not this effect, since it is converted into ferrous sulphide, and not iron, during the distillation.

**Preparation.**—The method used by Priestley is the most convenient. Either ammonium chloride or sulphate may be used. Thus :



The gas may be dried by passing over quicklime, and is collected by downward displacement of air, or over mercury.

In order to obtain a higher degree of purity the following procedure may be adopted. The gas, prepared as above, is first led over lime at a red heat, then absorbed in hydrochloric acid. The recrystallised ammonium chloride, now free from organic bases, is mixed with an

<sup>1</sup> Foxwell, *J. Soc. Chem. Ind.*, 1922, 41, 114T.

<sup>2</sup> See *The Carbonisation of Coal*, Lewes (Benn, 1918).

<sup>3</sup> Wolterek, *Compt. rend.*, 1908, 147, 460.

excess of pure lime, ground in a mortar, placed in a distillation flask and covered with calcium.<sup>1</sup> The neck of the flask is sealed. When heated, it evolves a steady stream of ammonia containing as impurities only air and water. This is then led through a long tube containing anhydrous barium oxide and potassium hydroxide, and finally over sodium wire to remove the last traces of water. The air and hydrogen are removed by fractional distillation under diminished pressure and at a low temperature.

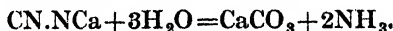
Pure ammonia is also obtained by gently heating sodium ammine, an addition compound which is obtained when metallic sodium is dissolved in liquid ammonia and is left as a red mass when the ammonia evaporates. Another method is to drop water on calcium or magnesium nitride in a suitable apparatus. The organic bases which are present in commercial ammonium salts may be destroyed by heating with nitric acid or permanganate. The remaining salt is then heated with lime as above.

Among other reactions by which ammonia or its salts are produced are the following :—

1. The reduction of compounds of nitrogen, such as nitrates or nitrites, with nascent hydrogen, produced, for example, from zinc and acid.

2. The acid hydrolysis of acid amides and other compounds containing the  $-\text{NH}_2$  and  $-\text{NH}-$  groups respectively.

3. The hydrolysis of the nitrides and cyanamides of metals, and of such non-metals as are electro-positive to nitrogen.<sup>2</sup> Thus ammonia is prepared in quantity by the hydrolysis of calcium cyanamide, which is first wetted, treated in large autoclaves with steam at 3 atmospheres to decompose any carbide which may be present, and then hydrolysed with steam at 11 atmospheres and  $180^\circ \text{C}$ . Thus :



4. Direct combination of nitrogen and hydrogen (see p. 95 *seq.*).

5. Decomposition of many organic compounds containing nitrogen in the presence of concentrated sulphuric acid, and the other substances specified in the Kjeldahl analysis for combined nitrogen.

**Physical Properties.**—*Density.*—The earlier determinations gave rather low results. A more exact value, 0.5967 (air=1), found by Biot and Arago, was afterwards corrected to 0.5971.<sup>3 4</sup> The weight of 1 litre of air at N.T.P. varies between 1.2927 and 1.2933 grams (see this series, Vol. VII., Part I.). The corresponding mean weight of a "normal litre" of ammonia is 0.7708 grams. Since the density of air relatively to hydrogen is 14.44, that of ammonia is 8.624, and the calculated molar weight is 17.4 ( $\text{O}_2=32$ ), which is greater than the true molar weight, 17.032, on account of the low value of the product  $p_v$  for ammonia at N.T.P. As in the case of other easily condensable gases, the compressibility at ordinary temperatures and moderate pressures is greater than that which corresponds to Boyle's Law. The product  $p_v$  increases

<sup>1</sup> Moser and Herzner, *Monatsh.*, 1923, 44, 115.

<sup>2</sup> A very pure product, containing only a trace of hydrogen as impurity, is obtained by allowing the nitrides of calcium or magnesium to drop into water (Moser and Herzner, *Monatsh.*, 1923, 44, 115).

<sup>3</sup> Leduc, *Compt. rend.*, 1897, 125, 571.

<sup>4</sup> Guye and Pintza, *ibid.*, 1908, 141, 51.

with diminution of pressure; if that at  $p=1$  atmosphere is taken as 1 (at  $10^{\circ}\text{C.}$ ), at a  $\frac{1}{2}$  atmosphere it becomes  $1.00632$ .<sup>1, 2</sup>

Hence the value of  $a$ , as given by the equation

$$a = \frac{p_0 v_0 - pv}{p_0 v_0 (p - p_0)},$$

is  $0.01264$ <sup>1</sup> or  $0.01257$ .<sup>2</sup>

The coefficients " $a$ " and " $b$ " of van der Waal's equation, which express the deviation from the gas laws in terms of a coefficient of molecular attraction and of the volume occupied by the molecules respectively, are 13,800 and 2.11 (see this series, Vol. I.).

**Thermal Expansion.**—The coefficients of expansion " $\alpha$ " are as follows over the temperature intervals specified:—<sup>3</sup>

$t^{\circ}\text{C.} = -20$ to $0$	$0$ to $50$	$0$ to $+100$
$\alpha = 0.003914$	$0.003854$	$0.003847$

### SPECIFIC HEATS OF AMMONIA.

Temperature, $^{\circ}\text{C.}$	Molar Heat at Constant Pressure, $C_p$ , or at Constant Volume, $C_v$ .	Authority.
0	$C_p = 8.54$	Wiedemann, <i>Pogg. Annalen</i> , 1895, 157, 1.  Partington and Shilling, <i>The Specific Heats of Gases</i> (Benn, 1924).  Voller, <i>Diss. Berlin</i> , 1908. Budde, <i>Zeitsch. anorg. Chem.</i> , 1912, 78, 159.
100	$C_p = 8.9$	
200	$C_p = 9.59$	
15	$C_p = 8.74$	
18	$C_v = 6.64$	Voller, <i>Diss. Berlin</i> , 1908. Budde, <i>Zeitsch. anorg. Chem.</i> , 1912, 78, 159.
1127	$C_v = 11.82$	
1927	$C_v = 21.42$	

The ratio of the specific heats has been determined at various temperatures with the following results:—

### RATIO OF SPECIFIC HEATS, $\frac{C_p}{C_v}$ or $\gamma$ .

Temperature, $^{\circ}\text{C.}$	Value of $\gamma$ .	Authority.
0 to 100	1.26 to 1.32	Wullner, <i>Wied. Ann.</i> , 1885, 24, 454. Muller, <i>Ber.</i> , 1883, 16, 214. Muller, <i>ibid.</i> , 1885, 18, 94. Partington and Cant, <i>Phil. Mag.</i> , 1922, [6], 43, 369. Schweckert, <i>Ann. Physik</i> , 1914, [4], 45, 913. Schöler, <i>ibid.</i> Schöler, <i>ibid.</i>
14.5	1.30	
20	1.30	
20 ( $\frac{1}{2}$ atm.)	1.30	
20 ( $3\frac{1}{2}$ atm.)	1.41	

<sup>1</sup> Rayleigh, *Phil. Trans.*, 1905, 204, 351.

<sup>2</sup> Jaquerod and Scheuer, *Compt. rend.*, 1905, 140, 1384.

<sup>3</sup> Perman, *Proc. Roy. Soc.*, 1906, 78, [A], 28.

The change of specific heat with temperature has been the subject of much investigation in connection with the nitrogen-hydrogen synthesis. As is usual with polyatomic gases the increase is rapid, and is expressed by an equation of the form

$$C_p = a + bT + cT^2.$$

The following equations have been suggested :—

$$C_p = 7.928 + 0.00361T - 0.05590T^2 + 0.0872T^3 \quad . \quad . \quad (1)^1$$

$$C_p = 8.045 + 0.0007T + 0.0551T^2 \quad . \quad . \quad . \quad (2)^2$$

$$C_p = 7.561 + 0.00373T + 0.05144T^2 \quad . \quad . \quad . \quad (3)^3$$

$$C_p = 8.686 + 0.00452t + 0.05144t^2 \quad . \quad . \quad . \quad (4)$$

$$C_p = 6.650 + 0.00465t + 0.05135t^2 \quad . \quad . \quad . \quad (5)$$

Equations (3), (4), and (5) are deduced from the most probable value of  $C_p$  at 15°, and from the value of  $\Sigma C_p(\frac{3}{2}H_2 + \frac{1}{2}N_2 - NH_3)$ , which, when introduced into the Kirchhoff equation,

$$\frac{dQ_p}{dt} = \Sigma nC_p$$

and

$$\frac{d \log K_p}{dt} = Q_p/RT^2 \text{ (integrated forms),}$$

satisfies the experimental values of  $Q_p$  and  $K_p$ .

The viscosities  $\eta$  of ammonia and air are given in C.G.S. units, those in brackets being calculated with the aid of Sutherland's constant, which for air is 117 and for ammonia is 370.

### VISCOSITIES OF AMMONIA AND OF AIR.

Temperature, °C.	$\eta \times 10^4$ Air.	$\eta \times 10^4$ Ammonia.	Authority.
0	1.724	(0.943)	Rankine and Smith, <i>Phil. Mag.</i> , 1921, [vi], 42, 601.
15	1.799	..	
100	2.191	1.303	

From these results it may be deduced that the collision area, namely,  $4\pi r^2$ , of the ammonia molecule is  $0.64 \times 10^{-15}$  (cm.)<sup>2</sup>, and the diameter of the molecule is  $1.4 \times 10^{-8}$  cm.

**Refractivity.**—The refractive index,  $n_D$ , for the sodium line is 1.000373 according to Lorenz,<sup>4</sup> and 1.000379 according to Mascart.<sup>4</sup> Values have also been obtained at different wave-lengths  $\lambda$  as follows :—

Wave-length, $\lambda$ , ( $m\mu$ )	= 436	546	656	480	546	671
Refractivity as $(n-1) 10^6$	= 396 <sup>5</sup>	387 <sup>5</sup>	382 <sup>5</sup>	383 <sup>6</sup>	379 <sup>6</sup>	374 <sup>6</sup>

The spectrum of ammonia consists of a bright central maximum at  $\lambda=336\mu\mu$ , a secondary maximum at 337.1, and a number of lines

<sup>1</sup> Nernst, *Zeitsch. Elektrochem.*, 1910, 16, 96.

<sup>2</sup> Haber, *ibid.*, 1914, 20, 597.

<sup>3</sup> Shilling, *Trans. Faraday Soc.*, 1926, 22, 396.

<sup>4</sup> Bruhl, *Zeitsch. physikal. Chem.*, 1891, 7, 25.

<sup>5</sup> Lorea and Patkowski, *Krak. Anz.*, 1913, p. 494.

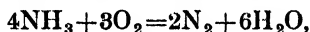
<sup>6</sup> C. and M. Cuthbertson, *Phil. Trans.*, 1913, 213, 1.

arranged in groups of three, which extend to a considerable distance in either direction. The spectrum is practically identical with the P group of the solar spectrum; hence the presence of ammonia in the absorbing atmosphere of the sun is definitely established.<sup>1</sup>

**Chemical Reactions.**—Ammonia is not oxidised by atmospheric oxygen or mild oxidising agents at ordinary temperatures, and even when ignited in air, the heat of combination is not sufficient to maintain a flame.<sup>2</sup> It will, however, burn vigorously in oxygen with a greenish yellow flame, forming water and nitrogen. A slow combustion is effected by passing sparks through a mixture of ammonia and air.<sup>3</sup> In this connection it is to be noted that ammonia itself is almost completely decomposed by the passage of electric sparks (see p. 62). It is also completely decomposed by ultra-violet light. When the gas, sealed into quartz tubes, is exposed to this light for six hours, the decomposition is so complete that no undecomposed gas can be detected by Nessler's reagent (see p. 94).<sup>4</sup>

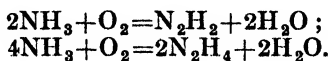
Oxidation proceeds at a much lower temperature in the presence of catalysts, and may then take a different course, leading to the formation of oxides of nitrogen, nitrous and nitric acids, and their ammonium salts. Among such catalysts are nickel, iron, copper, also manganates and permanganates.<sup>5, 6</sup> The most effective and useful catalyst is platinum; the finely divided metal accelerates the oxidation to water and nitrogen, while the smooth or compact metal leads to the oxides.<sup>7, 8, 9, 10</sup> This reaction has been studied<sup>11</sup> from the point of view of technical applications.<sup>12</sup> The first product of the reaction is probably nitric oxide, which is converted into the peroxide and then by water into the acids.<sup>13</sup>

The "preferential" combustion of the hydrogen in ammonia when a deficiency of oxygen is used may be represented by the equation:



which represents only the end-products. But the mechanism is considerably more complex, as is shown by the fact that free hydrogen is commonly found when there is a deficiency of oxygen, and oxides of nitrogen when there is an excess.

In the combustion of the theoretical quantities given above, 59 per cent. of nitrogen and 41 per cent. of hydrogen are found in the gaseous products.<sup>14</sup> This is accounted for by the intermediate formation of di-imide or hydrazine. Thus:



The results of the explosion of ammonia with electrolytic gas are somewhat similar. When the ratio of the gas to ammonia is higher than 3,

<sup>1</sup> Fowler and Gregory, *Proc. Roy. Soc.*, 1918, 94, [A], 470.

<sup>2</sup> Hofmann, *Annalen*, 1860, 115, 283.

<sup>3</sup> Observed by Henry, 1825.

<sup>4</sup> Coehn and Pringent, *Zeitsch. Elektrochem.*, 1914, 20, 275.

<sup>5</sup> du Motay, *Ber.*, 1871, 4, 891.

<sup>6</sup> Schwarz, *Dingl. poly. J.*, 1875, 218.

<sup>7</sup> Döbereiner, *Annalen*, 1832, 1, 29.

<sup>8</sup> Kuhlmann, *ibid.*, 1839, 29, 281.

<sup>9</sup> Schonbein, *J. prakt. Chem.*, 1857, 70, 129.

<sup>10</sup> Kraut, *Annalen*, 1865, 136, 69.

<sup>11</sup> Ostwald, *English Patent*, 698 (1902).

<sup>12</sup> Bayer & Co., *English Patent*, 18594 (1903).

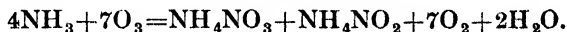
<sup>13</sup> Schmidt and Boeker, *Ber.*, 1906, 39, 1366.

<sup>14</sup> Muller, *Zeitsch. physikal. Chem. Unterr.*, 1913, p. 169.

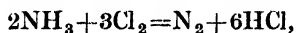
the ammonia is completely decomposed. When the ratio of ammonia to the gas is lower than 1.6, oxides of nitrogen are formed.<sup>1</sup>

Gaseous ammonia is oxidised to water and nitrogen by many oxides, as, for example, by copper oxide. Chlorine monoxide and iodine pentoxide oxidise it with separation of the halogen, selenium dioxide with separation of selenium.<sup>2</sup> Ammonia is also oxidised by oxides of nitrogen: when the gases are sparked or heated together, the hydrogen is oxidised and nitrogen is separated. The reaction in the case of nitrogen dioxide is violent even at lower temperatures.<sup>3</sup>

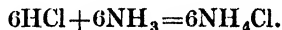
In aqueous solution, ammonia is oxidised at the anode during the electrolysis of its salts, also by powerful oxidising agents such as chlorine, bromine, ozone, hydrogen peroxide, chromates, and permanganates. The main product of oxidation is usually nitrogen. Under special conditions, and particularly in the presence of catalysts, nitrites or nitrates may be formed. This is the case, for example, during electrolytic oxidation in the presence of cupric oxide and alkali,<sup>4, 5</sup> or during oxidation by atmospheric oxygen in the presence of cupric oxide, also of metallic copper, iron, or zinc,<sup>6, 7</sup> or of hydrogen peroxide,<sup>8, 9</sup> or of moist ozone:



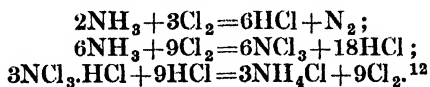
The more electro-negative non-metals, chlorine, bromine, and sulphur, readily combine with the hydrogen of ammonia. Thus chlorine oxidises ammonia to free nitrogen and ammonium chloride.<sup>10</sup> In the well-known lecture experiment by which the composition of ammonia is demonstrated, an excess of the latter is added to a measured volume of chlorine, and one-third of this volume of nitrogen is formed. Thus:



followed by



This reaction probably proceeds through the intermediate formation of  $\text{NCl}_3$ . Since the reaction takes place when both gases are anhydrous, the next step is not necessarily the hydrolysis of this compound, but rather consists in the intermediate production of  $\text{NCl}_3 \cdot \text{HCl}$ , which then reacts with hydrochloric acid, losing chlorine.<sup>11</sup> Thus:



<sup>1</sup> Partington and Prince, *Trans. Chem. Soc.*, 1924, 125, 2018.

<sup>2</sup> Ditte, *Bull. Soc. chim.*, 1870, [2], 13, 319.

<sup>3</sup> Besso and Rosset, *Compt. rend.*, 1906, 142, 633.

<sup>4</sup> Traube and Biltz, *Ber.*, 1904, 37, 3130; 1905, 38, 828.

<sup>5</sup> Muller and Spitzer, *ibid.*, 1905, 38, 718, 1188.

<sup>6</sup> Löw, *J. prakt. Chem.*, 1878, [2], 18, 298.

<sup>7</sup> Schonbein, *Ber. Akad. Ber.*, 1856, p. 580.

<sup>8</sup> Hoppe-Seyler, *Ber.*, 1883, 16, 1917.

<sup>9</sup> Weith and Weber, *ibid.*, 1874, 7, 1745.

<sup>10</sup> Hofmann, *Annalen*, 1860, 115, 283.

<sup>11</sup> Noyes and Haw, *J. Amer. Chem. Soc.*, 1920, 42, 2167; Noyes, *ibid.*, 1920, 42, 2173.

<sup>12</sup> According to the electron theories of valency,  $\text{NCl}_3$  is a covalent compound, the three chlorines being united by duplets, exactly as the hydrogens in ammonia; in both compounds the lone pair on the nitrogen atom is available for further combination, giving in the present case  $\text{NCl}_3 \cdot \text{HCl}$ . See also p. 14.



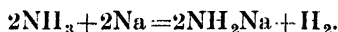
Iodine in aqueous solution gives  $\text{NH}_3\cdot\text{NI}_3$  (see p. 116). The vapour of phosphorus when passed with ammonia through a red-hot tube gives nitrogen and phosphine.<sup>1</sup> Sulphur vapour gives nitrogen and ammonium sulphide. Carbon at a red heat yields ammonium cyanide.<sup>2</sup> Boron combines with the nitrogen to form the very stable nitride, BN. The metals gold, platinum, silver, and copper decompose ammonia into its elements. Iron forms a nitride in addition, as also do chromium and other metals (see p. 48).

*Replacement of Hydrogen.*—Since ammonia is the hydride of a strongly electro-negative element, it might be supposed that at least one or perhaps two of the hydrogen atoms would exhibit an acidic character and be replaceable by metals. The resulting compounds, some of which are known, are called amides or imides respectively, and may be considered as salts when the metal is strongly electro-positive, although the same groups play a positive part in the amides and imides of non-metals, and of inorganic and organic acid radicals.

The amides of the metals may be formed under the following conditions :—

(1) By passing ammonia over the metal heated to a suitable temperature.

Thus, sodamide is prepared by passing a current of dry ammonia over sodium heated to between  $300^\circ$  and  $400^\circ$  C. in a nickel vessel :



It is a white solid which melts at  $155^\circ$  C. and is hydrolysed by water, giving ammonia and sodium hydroxide. The amides of potassium, rubidium, and barium may be made by this method (see this series, Vol. II.).

(2) By warming a solution of the metal in liquid ammonia. In these reactions an ammine, such as  $\text{KNH}_3$ ,  $\text{Ca}(\text{NH}_3)_4$ , is first formed (see this series, Vol. X.). On warming, substitution of hydrogen takes place. In this manner the following amides have been prepared :  $\text{NaNH}_2$ ,<sup>3</sup>  $\text{LiNH}_2$  and  $\text{Ca}(\text{NH}_2)_2$ ,<sup>4</sup>  $\text{KNH}_2$ .<sup>5</sup>

(3) By the action of ammonia on the hydrides. The amides of the alkali metals and barium have been prepared in this manner.<sup>6, 7</sup>

(4) Amides may also be prepared by double decomposition in liquid ammonia, notably silver amide,  $\text{AgNH}_2$ .<sup>7, 8</sup> Dry ammonia reacts with halides of many non-metals and their oxides (halanhydrides and halides of oxy-acids) as it does with those of organic acid radicals, giving amides and ammonium chloride. On further heating, these amides may pass into imides and nitrides, or these changes may take place quickly without any possibility of isolation of the intermediate compounds.<sup>9</sup>

<sup>1</sup> Bineau, *Ann. Chim. Phys.*, 1838, [2], 67, 225.

<sup>2</sup> Kuhlmann, *Annalen*, 1841, 38, 62; Langlois, *ibid.*, 1841, 38, 64; Weltzien, *ibid.*, 1864, 132, 224.

<sup>3</sup> Joannis, *Compt. rend.*, 1891, 112, 392.

<sup>4</sup> Moissan, *ibid.*, 1898, 127, 685.

<sup>5</sup> Franklin and Stafford, *Amer. Chem. J.*, 1902, 28, 83.

<sup>6</sup> Moissan, *Compt. rend.*, 1903, 136, 587.

<sup>7</sup> Ruff and Geisel, *Ber.*, 1905, 39, 828.

<sup>8</sup> Franklin, *Zeitsch. anorg. Chem.*, 1905, 46, 1.

<sup>9</sup> These compounds are usually described under Amides, etc., of the element in that volume of this series which deals with the appropriate group, e.g.  $\text{Si}(\text{NH}_2)_4$  and  $\text{Si}(\text{NH}_2)_3$  in Vol. V. The amides, imides, and nitrides of phosphorus, arsenic, and antimony are described in Part II. of this volume.

*Reactions with Acids.*—Ammonia forms salts in several ways, viz. :

(1) By direct addition of  $\text{NH}_3$  to a hydracid or oxy-acid.<sup>1</sup> The formation of salts by this method is best exemplified by the halides. Thus :



The solid salts are anhydrous ; they can be sublimed with dissociation in the vapour phase and recombination during condensation. Dibasic acids in excess give acid salts, such as  $\text{NH}_4\text{HSO}_4$ . Hydrogen fluoride behaves in this respect as a dibasic acid, and  $\text{NH}_4\text{F.HF}$  is formed by the extensive hydrolysis of the salt,  $\text{NH}_4\text{F}$ , on warming. Gaseous ammonia combines with gaseous carbon dioxide to give ammonium carbamate,  $\text{NH}_2\text{—CO—ONH}_2$ . With hydrogen sulphide, crystals of  $(\text{NH}_4)_2\text{S}$  are obtained at  $-18^\circ \text{C}$ .,<sup>2</sup> and of  $\text{NH}_4\text{HS}$  at  $0^\circ \text{C}$ .<sup>3</sup> Compounds of ammonia with weak acids are conveniently prepared by interaction in organic solvents. Thus,  $\text{NH}_4\text{IIS}$  has been prepared in dry alcohol and ether, and the crystalline alcoholate,  $(\text{NH}_4)_2\text{S.C}_2\text{H}_5\text{OH}$ , in alcohol.<sup>4</sup>

(2) By the neutralisation of aqueous ammonia with acids, and subsequent evaporation and crystallisation of the salts. The majority of ammonium salts may be prepared in this manner in aqueous solution.

(3) By double decomposition, with separation of a less soluble salt from the resulting salt-pair. Ammonium salts crystallise usually in an anhydrous condition on evaporation, and are more or less decomposed with loss of ammonia on long boiling (see this series, Vol. II.).

**The Decomposition of Ammonia.**—As has already been mentioned, the decomposition of ammonia into its elements, like its formation from these, is greatly accelerated by the presence of solid surfaces. Incandescent wires of various metals are particularly effective in this respect, no doubt on account of the fact that their surfaces adsorb hydrogen in an active, probably an atomic, form. This decomposition presents some points of interest in connection with the theories of heterogeneous, or gas-solid, surface reactions. On a tungsten wire at  $856^\circ \text{C}$ . the reaction is unimolecular at very low pressures—that is, it conforms to the requirements of the equation

$$-\frac{dc}{dt} = kc.$$

The active mass of the gas is that which is adsorbed on the surface, and it may be assumed that as long as this is not completely covered the active area is proportional to the pressure, i.e. to the concentration. At higher pressures—50 mm. or more—the reaction is found to be of zero order ; in other words, it is independent of the pressure in the gas phase ; under these conditions the surface is supposed to be completely covered.

<sup>1</sup> The ingredients must not be absolutely dry. See discussion on dissociation of  $\text{NH}_4\text{Cl}$  (this series, Vol. II.).

<sup>2</sup> Bineau, *Ann. Chim. Phys.*, 1838, 67, 230 ; 1838, 68, 435 ; 1839, 70, 261.

<sup>3</sup> Troost, *Compt. rend.*, 1879, 88, 1267.

<sup>4</sup> Thomas and Riding, *Trans. Chem. Soc.*, 1923, 123, 1181.

The decomposition of ammonia on a heated platinum wire at about  $1000^{\circ}\text{C}$ . proceeds with great velocity at first, then falls off rapidly as the hydrogen accumulates, and the reaction proceeds at a rate inversely proportional to its partial pressure. Thus :

$$\frac{d(\text{NH}_3)}{dt} = \frac{k[\text{NH}_3]}{[\text{H}_2]}.$$

This effect is not due to the active mass of the hydrogen in the homogeneous gas phase, but is connected with the fact that hydrogen is strongly adsorbed even at low pressures on the surface, which soon becomes saturated, and thus prevents the ammonia molecules from coming into direct contact with the reactive surface except through a layer of this hydrogen.<sup>1</sup>

#### LIQUID AMMONIA.

**History and Physical Properties.**—Ammonia was first liquefied by Faraday, who heated a compound of silver chloride and ammonia contained in one limb of a bent tube, the other limb being cooled in ice. Bunsen showed that it could be liquefied under atmospheric pressure in a good freezing mixture (ice and calcium chloride), and hence gave an estimate of its boiling-point, which has since been determined by many investigators.

#### BOILING-POINT OF ANHYDROUS AMMONIA.

Boiling-point, $^{\circ}\text{C}$ . at Normal Pressure.	Authority.
—33.46	Gibbs, <i>J. Amer. Chem. Soc.</i> , 1904, <b>27</b> , 851.
—33.2	Brill, <i>Drude's Annalen</i> , 1906, <b>21</b> , 170.
—33.5	Perman, <i>Proc. Roy. Soc.</i> , 1906, <b>78A</b> , 28.
—33.5	Baume and Perrot, <i>Arch. Sci. phys. nat. Genève</i> , 1911, <b>32</b> , 62.
—33.41	McKelvy and Taylor, <i>U.S. Bureau Standards</i> , 1923, 465.

The *melting-point* of solid ammonia has been variously given as :

$$-78.2^{\circ},^2 -77.7^{\circ},^3 \text{ and } -77.0^{\circ}\text{C}.^4$$

The *specific heat* of liquid ammonia has been determined with the following results :—

<sup>1</sup> Hinshelwood and Burk, *Trans. Chem. Soc.*, 1925, **127**, 1114, 1116.

<sup>2</sup> Baume and Perrot, *loc. cit.* (see Table).

<sup>3</sup> McKelvy and Taylor, *loc. cit.* (see Table).

<sup>4</sup> Brill, *loc. cit.* (see Table).

## SPECIFIC HEAT OF LIQUID AMMONIA.

Temperature Interval, ° C.	Specific Heat.	Auth. rity.
0 to +40	0.88 to 0.89	Ludecking and Starr, <i>Amer. J. Sci.</i> , 1893, 45, 200.
30 to +62	1.22876	v. Strombeck, <i>J. Frankl. Inst.</i> , 1891, p. 131.
0 to +30	1.0206	Elleau and Eunis, <i>J. Frankl. Inst.</i> , 1898, p. 145.
--188 to -103	0.50	Dewar, <i>Proc. Roy. Soc.</i> , 1905, A76, 375.
-40	1.054	Osborne and van Dusen, <i>J. Amer. Chem. Soc.</i> , 1918, 40, 1.
0	1.099	
+40	1.162	
0 to +20	1.152	Keyes and Babcock, <i>J. Amer. Chem. Soc.</i> , 1917, 39, 1524.
+20 to +50	1.172	
+30	1.168	Babcock, <i>Proc. Amer. Acad.</i> , 1920, 55, 523.
50	1.222	
70	1.297	
90	1.131	
100	1.538	

According to Dieterici,<sup>1</sup> the specific heats between 0° and 70° C. are :

t° C.	= 0	10	20	30	40	50	60	70
Spec. heat.	= 1.118	1.140	1.161	1.181	1.203	1.225	1.247	1.269

## DENSITIES OF LIQUID AMMONIA AND ITS SATURATED VAPOUR.

Temperature, ° C. =	-50	-40	-30	-20	-10		
Density <sup>2</sup>	= 0.6954	0.6835	0.6715	0.6593	0.6469		
Temperature, ° C. =	0	+10	+20	+40	+60	+80	+100
Density <sup>2</sup>	= 0.6341	0.6207	0.6067	0.5756	0.5404	0.5004	0.4522
Density <sup>3</sup>	= 0.6388	0.6248	0.6103	0.5796	0.5458	0.5079	0.4626

The isobaric volumes and densities of liquid and vapour under a pressure equal to that of the vapour have been determined by Dieterici <sup>1</sup> and Berthoud.<sup>4</sup>

## ISOBARIC SPECIFIC VOLUMES OF LIQUID AMMONIA AND ITS VAPOUR.

(Dieterici.)

Temperature, ° C. =	0	+10	+20	+30	+40	+50	+60	+70	+80	+90	+100
v <sub>L</sub>	= 1.5656	1.5985	1.6342	1.6765	1.7227	1.7719	1.8250	1.8875	1.9595	2.0390	2.1525
v <sub>V</sub>	= 294.0	206.0	148.0	108.5	80.9	62.3	48.6	37.8	30.2	24.4	17.05

<sup>1</sup> Dieterici, *Zeitsch. Kalteind.*, 1904, p. 1.Lange, *ibid.*, 1898, 5, 39.<sup>2</sup> Drewes, *Dissertation*, Hannover, 1903.<sup>4</sup> Berthoud, *Helv. Chim. Acta*, 1918, 1, 84.

# ISOBARIC DENSITIES OF LIQUID AMMONIA AND ITS VAPOUR.

(Berthoud.)

Temperature, ° C.	0	+45.0	78.7	98.75	109.2	116.4	121.3	123.2	125.4	129.6
$D_{15}$	0.6389	.5696	.5120	.4640	.4339	.4056	.3831	.3750	.3584	.3246
$D_v$	0.0034	.0150	.0322	.0533	.0691	.0873	.1024	.1085	.1220	.1509

The *vapour pressures* of liquid ammonia were first determined by Faraday, and afterwards by Bunsen, Pictet, and others,<sup>1</sup> but their results are now merely of historical interest.

These constants have been redetermined with great accuracy by methods which deserve mention, as they are widely used in similar cases. The apparatus is described in a paper by Cragoe, Meyers, and Taylor.<sup>2</sup> A static method was employed. The pressures were read on mercury manometers, the whole being immersed in thermostats containing gasoline which could be regulated to 0.01° C.; or better, at the lower temperatures by means of coils in which carbon dioxide was allowed to expand. It was shown that the presence of uncondensable gases caused lag in the attainment of the equilibrium pressures. Therefore the greatest care was taken to purify the ammonia. A large quantity of synthetic ammonia was distilled twice, the middle portion of the second distillate was allowed to stand in contact with metallic sodium for about a week, the liquid was shaken and hydrogen blown off. After several distillations in a high-pressure apparatus, the middle fraction being retained each time, the ammonia was frozen several times in liquid air, all uncondensed gases were pumped off, and during the periods of liquefaction some vapour was allowed to escape. Finally a product was obtained which contained less than 1 in 100,000 of uncondensable gases and less than 0.003 per cent. of water. The boiling-point of this ammonia by the static method was -33.354° C.; by the ordinary method, using a Beckmann thermometer, it was -33.341° C.

## VAPOUR PRESSURES OF LIQUID AMMONIA.

(Cragoe, Meyers, and Taylor, 1920.)

Temperature, ° C.	-78.0	-64.0	-51.0	-48.0	-44.0	-40.0	-38.87	-33.354
Pressure (mm.)	44.0	125.29	289.43	345.03	432.98	538.58	571.77	760.0
t° C.	-30.0	-25.0	-20.0	-15.0	-10.0	-5.0	0.0	5.0
p (mm.)	897.2	1137.4	1427.0	1772.8	2181.6	2661.5	3220.8	3867.9
t° C.	10.0	15.0	20.0	25.0	30.0	40.0	45.0	50.0
p (mm.)	4612.1	5462.6	6428.2	7520.5	8750.9	11661.4	13362.3	15245.4
t° C.	55.0	60.0	65.0	70.0				
p (mm.)	17325.3	19606.0	22108.5	24836.8				

These results and others can be expressed by the interpolation formulæ:—

<sup>1</sup> Brill, *loc. cit.*, p. 4; Regnault, *Mém. Inst. France*, 1862, 26, 596.

Cragoe, Meyers, and Taylor, *J. Amer. Chem. Soc.*, 1920, 42, 206.

$$\log_{10} p = 30.256818 - \frac{1914.0569}{T} - 8.4598324 \log T + 2.39309 \times 10^{-3} T + 2.955214 \times 10^{-6} T^2 \quad (1)$$

$$\log_{10} p = 12.463400 - \frac{1648.6068}{T} - 0.01638646 T + 2.403276 \times 10^{-5} T^2 - 1.168708 \times 10^{-8} T^3 \quad (2)$$

These and the preceding data have much value in industry, since liquid ammonia is frequently used as a refrigerant. It is a convenient working substance for reversed heat engines, the latent heat of vaporisation and expansion through coils being absorbed by the brine of cold-storage rooms, etc. The gas, when used commercially, is dried with quicklime, and is kept in gasometers over petroleum oil; it is usually compressed in two stages, first to 3 or 4 atmospheres, then to liquefy at about 8 atmospheres.

**Critical Constants.**—The critical temperature is variously given as  $130^\circ$ ,<sup>1</sup>  $131^\circ$ ,<sup>2</sup>  $132.3^\circ$ ,<sup>3</sup> and  $132.9^\circ$ ,<sup>7</sup> C., the critical density as  $0.2362$ ,<sup>3</sup> the critical volume as  $4.234$ ,<sup>3</sup> and the critical pressure as  $115$ ,<sup>1</sup>  $113$ ,<sup>2</sup> and  $112.3$ ,<sup>7</sup> atmospheres respectively.

**Surface Tension  $\sigma$ .**—

Temperature, ° C.	11.10	34.05	58.98
$\sigma$	23.38	18.05	12.95

**Adsorption by Charcoal** (see also this series, Vol. V.).—At ordinary temperatures 1 gram of charcoal adsorbs nearly 200 c.c. of ammonia (178 c.c., Kayser<sup>4</sup>). The amount adsorbed at atmospheric pressure increases with fall of temperature. At each temperature the volume “ $v$ ” varies with the pressure according to the equation

$$v = ap^{\frac{1}{n}},$$

in which  $a$  and  $n$  are constants. This equation expresses the behaviour of ammonia from  $-20^\circ$  to  $+200^\circ$  C.,<sup>5</sup> and is known as the adsorption isotherm. The heat of adsorption, 494 Cals. per gram of ammonia, is nearly twice as great as the latent heat of condensation to liquid.<sup>6</sup>

**Latent Heat.**—This is usually taken as 5.000 Cals. per mol. This is higher than the value obtained by the differentiation of equation (1) above, which gives 3.950 Cals.

**Molecular Complexity.**—The boiling-point of ammonia, considered as the first member of the series  $\text{NH}_3$ ,  $\text{PH}_3$ , etc., is abnormally high, just as that of  $\text{OH}_2$  is high in relation to those of  $\text{SH}_2$ , etc. This as well as other peculiarities in the properties of liquid ammonia (see also p. 76), which it shares with water, are in both cases attributed to association of the liquids.

The value of the Despretz-Young-Trouton ratio, namely, the latent heat of vaporisation divided by normal boiling-point on the absolute

<sup>1</sup> Dewar, *Phil. Mag.*, 1884, [5], 18, 210.

<sup>2</sup> Vincent and Chappuis, *J. Physique*, 1886, [2], 5, 58.

<sup>3</sup> Berthoud, *Helv. Chim. Acta*, 1918, 1, 84.

<sup>4</sup> Kayser, *Wied. Annalen*, 1881, 12, 526.

<sup>5</sup> Richardson, *J. Chem. Soc.*, 1917, [A ii], 526.

<sup>6</sup> Favre, *Ann. Chim. Phys.*, 1874, [5], 1, 209.

<sup>7</sup> Cardoso and Giltay, *J. Chim. Phys.*, 1912, 10, 516.

scale, may be calculated from the equations of Cragoe, Meyers, and Taylor. It is 19.7. This is not far from the normal value, 20 to 22. It has been shown by Nernst<sup>1</sup> that this constant is really a function of the temperature, and that in the case of many gases

$$\frac{Q}{T_b} = 9.5 \log T_b - 0.007 T_b.$$

Thus, at a boiling-point of 239.65, the normal constant will be 21. A slight degree of association is thus indicated.

The temperature coefficients of molar surface energy are 1.80 and 1.79 (*vide supra*). The corresponding value for a normal liquid being 2.12, the coefficient of association is 1.27.

The critical density, 0.2362, is 4.211 times the theoretical density, as deduced by a strict application of the gas laws to the critical conditions. The ratio in the case of normal liquids is about 3.6.

**General Properties and Comparison with Water.**—A comparison between liquid ammonia and water in respect of physical properties, and its action as a solvent, reveals many interesting similarities. These are summarised in the following table :—

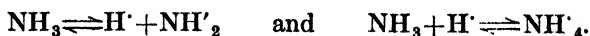
#### COMPARISON OF AMMONIA WITH WATER.

	NH <sub>3</sub> .	H <sub>2</sub> O.
Melting-point, ° C.	—77	0
Boiling-point, ° C.	—38.5	+100
Density at 20° C.	0.61	0.9982
$T_c$	273+181 abs.	273+374 abs.
$p_c$	113 (atm.)	218 (atm.)
Molar elevation of B.P. (100 grams)	3.4 (lowest known)	5.2
Heat of fusion	1.838 Cals.	1.440 Cals.
Dielectric constant	c. 21–23	81.7
Surface tension	25	28
Viscosity	$2.6 \times 10^{-3}$ } (at its b.p.) }	$10.6 \times 10^{-3}$ } (at 18°) }
Factor of association	1.27 (from surface tension)	3.0 (from surface tension)
Refractive index	1.33	1.33

It will be observed that the fluidity is much greater (about four times) than that of water, and the surface tension appreciably lower, both being measured at ordinary temperatures. The various physical data lead to the conclusion that ammonia, like water, is probably associated in the liquid state. Like other pure liquids, ammonia is capable of conducting the electric current : its conductivity, although very small, has a definite limit, below which it is not diminished by the highest possible

<sup>1</sup> Nernst, *Experimental and Theoretical Applications of Thermodynamics to Chemistry* (Constable, 1907), Lecture X.

purification. As in the case of water, this is attributed to a very slight electrolytic dissociation :



The dielectric constant is high, but far inferior to that of water. The refractive index is nearly the same as that of water. Ammonia also resembles water in showing some deep absorption bands in the infra-red between the wave-lengths  $9\mu$  and  $13\mu$ . This is probably connected with its high ionising power as a solvent.<sup>1, 2</sup>

**Solvent Properties.**—Liquid ammonia is one of the most comprehensive solvents known. It dissolves non-metals, iodine, sulphur, and phosphorus, also many halides and sulphides of the non-metals which are insoluble in water or are hydrolysed by it. The metals of the alkalis and alkaline earths are freely soluble, and the solutions are good conductors of electricity (see below, p. 80). The solubility of potassium in 100 grams of liquid ammonia is 48.75 at  $0^\circ \text{C}$ ., that of sodium 23.2 at  $0^\circ$ , 24.5 at  $-30^\circ$ , and 22.0 at  $22^\circ \text{C}$ .<sup>3</sup> At such high concentrations the ammonia pressures are greatly reduced and may lie far below one atmosphere at ordinary temperatures. In the case of lithium two liquid phases are formed, having an ammonia pressure of 540 mm. The saturated solution, having an ammonia pressure of 3.61 mm., contains 11.4 grams of lithium in 100 grams of ammonia.<sup>4</sup> Ammonia dissolves many typical aqueous electrolytes, such as salts. The following are insoluble: oxides, hydroxides, and sulphides of the metals; also fluorides, sulphates, sulphites, phosphates, arsenates, carbonates, and oxalates. The solubilities of other salts, especially of ammonium salts, is often high. That of ammonium nitrate, which is zero at  $-80^\circ \text{C}$ ., increases rapidly with rise of temperature.

	$t^\circ \text{C.} = -80$	$-30$	$0$	$+33.3$
Grams of $\text{NH}_4\text{NO}_3$ in 100				
grams of $\text{NH}_3$ . . . . .	$= 0$	224	291	398

Dry ammonium thiocyanate cooled by ice absorbs 45 per cent. by weight of ammonia, which, however, evolves it again on heating.<sup>5, 6</sup> Such solutions have been used in small refrigerators, working somewhat on the principle of the Carré freezing machine (see this series, Vol. V.).

Salts of the following acid radicals usually dissolve in liquid ammonia, namely, nitrates, iodides, bromides and chlorides, cyanides and thiocyanates. Other soluble substances are amides, such as  $\text{KNH}_2$ , non-electrolytes such as  $\text{Hg}(\text{CN})_2$ , and various complexes such as  $\text{K}_2\text{Hg}(\text{CN})_4$ , which often have the same composition as the corresponding complex salts which are formed in water.<sup>7</sup> Many organic compounds will dissolve, among which may be mentioned amides, nitro compounds, the free alkyl ammonium bases, their hydroxides, and salts (p. 80).

Ammonia has been used as a solvent in the determination of molar

<sup>1</sup> Paschen, *Wied. Annalen*, 1894, 52, 209.

<sup>2</sup> Abney and Festing, *Phil. Mag.*, 1882, 172, 887.

<sup>3</sup> Ruff and Geisel, *Ber.*, 1906, 39, 838.

<sup>4</sup> Kraus and Johnston, *J. Amer. Chem. Soc.*, 1925, 47, 725.

<sup>5</sup> Kuriloff, *Zeitsch. physikal. Chem.*, 1898, 25, 109.

<sup>6</sup> Foote and Brinkley, *J. Amer. Chem. Soc.*, 1921, 43, 1178.

<sup>7</sup> Franklin, *Zeitsch. physikal. Chem.*, 1909, 69, 272.

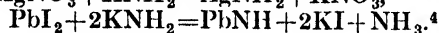
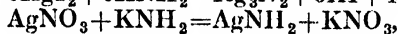


weights. The molar elevation of the boiling-point (100 grams solvent), calculated from the thermal constants, is 3.4. This agrees with the experimental elevation in the case of some solutes, *i.e.* those which have a normal molar weight.<sup>1</sup> As in the case of aqueous solutions, however, the molar weight found often differs from the formula weight. When the constant, or molar elevation of the boiling-point, calculated from the experimental elevation on the assumption of simple molecules, is higher than the theoretical constant, the solute is regarded as dissociated, as in the case of salts and some organic compounds, or else it is assumed to be associated with solvent molecules to give an ammine.

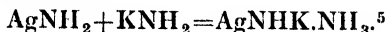
The molar weight of the solute may also be determined from the lowering of the vapour pressure. The molar weight of sodium found thus decreases nearly as a linear function of the concentration and does not reach a definite limit. It is only possible to state <sup>2</sup> that the limit will be below 23.

The cryoscopic constant of ammonia, as experimentally determined, is about 14, whereas the value calculated from the thermal constants is 9.4.<sup>3</sup>

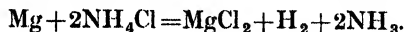
**Reactions in Liquid Ammonia.**—The ions which are present in these electrolytically conducting solutions react and give precipitates, etc., which are sometimes of an unusual kind and would be difficult to produce in any other solvent. Dissolved metals may interact to give alloys; thus, in the case of sodium and lead, an alloy of composition represented by  $\text{NaPb}_{2.25}$  is precipitated. The lead is the negative constituent, as it is precipitated on the anode during electrolysis. Sodium and tellurium give insoluble  $\text{Na}_2\text{Te}$  and soluble  $\text{Na}_2\text{Te}_2$ . Simple and complex amides and nitrides may be formed by double decomposition, *e.g.*:



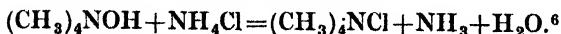
Aluminium iodide with potassamide gives first  $\text{Al}(\text{NH}_2)_3 \cdot \text{AlI}_3$ , then  $\text{Al}(\text{NH}_2)_3 \cdot \text{Al}(\text{NH}_2)_2\text{I} \cdot \text{NH}_3$ . Cadmium thiocyanate, with the same reagent, gives  $\text{Cd}(\text{NH}_2)_2$ , a white powder which acts violently on water and explodes when heated. Silver amide with potassamide gives crystals containing ammonia:



Magnesium dissolves in a solution of ammonium chloride in liquid ammonia. Here the ammonium ion plays the part of the hydron in acid aqueous solutions, and is displaced by the magnesium:



The strongly basic alkyl ammonium hydroxides displace the ammonia from its salts, as they do in aqueous solution:



<sup>1</sup> Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 820.

<sup>2</sup> Kraus, *J. Amer. Chem. Soc.*, 1907, 29, 1557; 1908, 30, 1197; 1914, 36, 864; 1921, 43, 749.

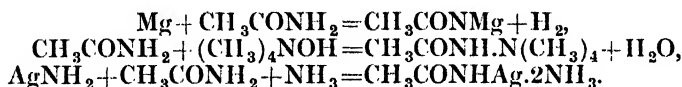
<sup>3</sup> Reihlen and Nestle, *Ber.*, 1926, 59, B1159.

<sup>4</sup> Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 820.

<sup>5</sup> Franklin, *ibid.*, 1915, 37, 847.

<sup>6</sup> Franklin, *ibid.*, 1912, 34, 285.

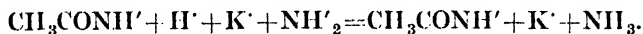
Since in ammonia the  $-\text{NH}_2$  group may be regarded as taking the place of the  $-\text{OH}$  in water, acid amides in ammonia correspond to carboxylic acids in water, and the former have therefore been named "ammono-acids" by Franklin.<sup>1</sup> They are dibasic acids, capable of ionising in two stages into  $\text{RCONH}^+ + \text{H}^-$  and  $\text{RCON}'' + 2\text{H}^-$ . The ionisation is in some cases considerable, as shown by the conductivities. Typical reactions of the ammono-acids are :



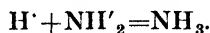
In water, acid amides do not dissociate but add on the hydron of acids, and therefore behave as (weak) bases. The amides of bases have been called by Franklin "ammono-bases." These will react with ammono-acids thus :



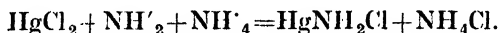
or



As in the case of the neutralisation of an acid by an alkali in water, the ionic part of the reaction consists in the formation of undissociated solvent :



Just as salts of weak bases are hydrolysed by the substitution of OH for halogen, etc., so they may be "ammonolysed" by the substitution of NH<sub>2</sub> :

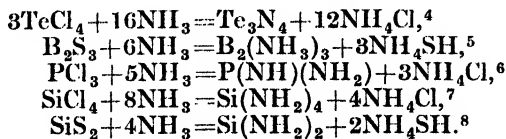


The amido-chloride is insoluble in ammonia as it is in water.

Ammonolysis is, however, much less common than hydrolysis. Most salts dissolved give clear solutions in ammonia, while ammonolysis would give precipitates.

The ammono-salts of the alkali metals are also obtained by reactions in liquid ammonia. Thus, dipotassium ammono-sodiate,  $\text{Na}(\text{NH}_2)_3\text{K}_2$ , is prepared by the action of sodium on potassanide, both dissolved in ammonia, in the presence of platinum black.<sup>2, 3</sup>

Amides and nitrides of the non-metals are often formed by the ammonolysis of the chloranhydrides and sulphides in liquid ammonia :



<sup>1</sup> Franklin, *Amer. Chem. J.*, 1912, 47, 285.

<sup>3</sup> Franklin, *J. Physical Chem.*, 1919, 23, 36.

<sup>5</sup> Stock and Poppenberg, *Ber.*, 1901, 34, 399.

<sup>6</sup> Joannis, *Compt. rend.*, 1904, 139, 364.

<sup>7</sup> Lengfeld, *Amer. Chem. J.*, 1899, 21, 531.

<sup>8</sup> Blix and Wirbelauer, *Ber.*, 1903, 36, 4220.

<sup>2</sup> See this series, Vol. III.

<sup>4</sup> Metzner, *Compt. rend.*, 1897, 124, 32.

**Electrical Properties of Solutions in Ammonia.**—The electrical conductivity of pure ammonia is very low, and in this case the difficulty of avoiding traces of water are very great. Hence the older values of this constant are higher than the more recent, namely,  $0.1 \times 10^{-7}$  reciprocal ohms.<sup>1, 2, 3, 4</sup>

Besides the ions  $H^+$ ,  $NH_4^+$ , and  $NH_2^+$ , the anions  $NH_2^-$  and  $N^-$  may possibly be present. Three inflections have been found on the curve of anodic polarisation against current, which may correspond to the discharge of these ions. In accordance with its character as a dissociating solvent, liquid ammonia has the relatively high dielectric constant of 21 to 23,<sup>1</sup> which is inferior only to those of some alcohols and nitriles, e.g. benzonitrile, 26.0, and to that of water, 81.45.<sup>5</sup> In the case of ammonia, as in that of water, there are two types of solutions: those of salts which have a limiting conductivity at limiting dilution, but do not give a dissociation constant, i.e. do not obey the dilution law; and those of organic compounds of a polar type, which do not give a limiting equivalent conductivity but do obey the dilution law.<sup>6</sup> As an example of the first class we may take  $KNO_3$ . The equivalent conductivities,  $\lambda$ , and degrees of dissociation,  $\alpha$ , at  $-33^\circ C$ . and various dilutions,  $V$  (litres per mol.), are as follows:—

$V = 324$	1001	2514	6162	23060	69820	$\infty$
$\lambda = 192.7$	245.0	282.7	309.9	330.1	338.6	$339 = \lambda_0$
$\alpha = 0.567$	0.720	0.831	0.912	0.972	0.995	1.00

The equivalent conductivities are higher than in water at corresponding and at infinite dilutions, but the degrees of dissociation at corresponding dilutions are lower. The following equivalent conductivities are additively made up of a term due to each ion:—

Salt.	$KNO_3$ .	KBr.	$NaNO_3$ .	NaBr.	$NH_4NO_3$ .	$NH_4Br$ .	$LiNO_3$ .	$AgNO_3$ .
$\lambda_0 =$	339	340	301	302	302	303	283	287

Since the transport numbers of salts in ammonia have been determined, the ionic conductivities can be calculated and prove to be about three times the conductivities in water.<sup>6, 7</sup>

Kation.	Li.	Na.	K.	$NH_4$ .	Ag.
$L_0$ in $H_2O$ ( $18^\circ C$ .) =	33.8	48.4	64.5	64.7	54.0
$L_0$ in $NH_3$ (at b.p.) =	112	180	168	181	116

Anion.	Cl.	Br.	I.	$NO_3$ .
$L_0$ in $H_2O$ ( $18^\circ C$ .) =	65.5	67.7	66.6	61.8
$L_0$ in $NH_3$ (at b.p.) =	179	172	171	171

<sup>1</sup> Goodwin and Thompson, *Physical Review*, 1899, 8, 38.

<sup>2</sup> Cady, *J. Physical Chem.*, 1896, 1, 707.

<sup>3</sup> Frenzel, *Zeitsch. Elektrochem.*, 1900, 6, 486.

<sup>4</sup> Franklin and Kraus, *Amer. Chem. J.*, 1900, 23, 277.

<sup>5</sup> Lattey, *Phil. Mag.*, 1921, 41, 829.

<sup>6</sup> Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, 35, 1337.

<sup>7</sup> Franklin and Cady, *J. Amer. Chem. Soc.*, 1904, 26, 449.

The differences between individual ions, especially anions, are much less marked in ammonia than in water. The higher conductivities are no doubt connected with the lower viscosity (or higher fluidity) of ammonia, since the resistance to the motion of the ions is some function of the viscosity. That of water at 18° C. is  $10.63 \times 10^{-3}$ , while that of ammonia at its boiling-point is  $2.56 \times 10^{-3}$ .<sup>1</sup>

In the case of the slowest ions, the ratios of ionic conductivity to fluidity are about 0.8 in both solvents.

In very dilute solutions of salts, and in rather dilute solutions of other compounds (see below), a mass action constant may be calculated, but in order to express the behaviour in more concentrated solutions other constants must be introduced, as in the equation of Kraus and Bray :

$$K' = \frac{(aC)^2}{(1-a)C} = D(aC)^m + K.$$

Nitromethane, thiobenzamide, orthonitrophenol, methylnitramine, trinitrobenzene, trinitraniline are among the organic compounds which are electrolytes in ammonia and obey the law of mass action moderately well. The following are typical constants :—

	10 <sup>4</sup> k.	m.	D.	λ <sub>0</sub> .
Potassamide . . .	1.20	1.18	0.095	801
Trinitraniline . . .	30.0	0.73	0.38	234

Liquid ammonia is a favourable medium for the preparation of free "ammonium" and the alkyl substituted ammonium radicals. The radical N(CH<sub>3</sub>)<sub>4</sub> has been precipitated in the free state at the cathode during the electrolysis of the salt dissolved in liquid ammonia, in which it is soluble, giving a solution somewhat similar to that of potassium. When compressed it is a good conductor of electricity. The radical HgCH<sub>3</sub> can be freed from HgCH<sub>3</sub>Cl by washing with liquid ammonia. It decomposes at ordinary temperatures into Hg(CH<sub>3</sub>)<sub>2</sub> and Hg.<sup>2, 3, 4</sup>

**Electrochemistry of Metallic Solutions.**—Solutions of the alkali metals are blue when dilute; they assume a metallic lustre and become reflecting when more concentrated. There is little chemical action; the amides are only formed to a slight extent, so that it must be supposed that the metal is dissolved as such, and that the high conductivity is not due to ordinary ions. During electrolysis there are none of the usual appearances at the electrodes, such as the separation of solids or gases. The conduction in this respect resembles that of a metal. The dissolved metal is associated with the kation, since it may be completely transferred into the katholyte by electrolysis. The negative carrier is probably the electron. The equivalent conductivity (referred in the usual manner to the solute, *e.g.* dissolved sodium) is high; it reaches a minimum at a dilution of between 20 and 80, and then increases greatly with increase of concentration :

V=0.5047	1.088	13.86	30.4	690.1	37880
λ = 82490	3228	478.3	478.5	869.4	1034

<sup>1</sup> Fitzgerald, *J. Physical Chem.*, 1912, 16, 621.

<sup>2</sup> Palmaer, *Zeitsch. Elektrochem.*, 1902, 8, 729.

<sup>3</sup> Kraus, *J. Amer. Chem. Soc.*, 1913, 35, 1732.

<sup>4</sup> McCoy and Moore, *ibid.*, 1911, 33, 273.

The specific conductivity  $= \frac{\lambda}{1000 V}$  obviously increases still more rapidly with increasing concentration, and the atomic conductance approaches that of the metal itself, as is seen from the results in still more concentrated solutions: <sup>1</sup>

V=1.674	0.9265	0.5099	0.3230	0.1081
x=1.298	5.988	148.3	714.0	5047.0

The atomic conductance of a saturated solution is  $1.1 \times 10^6$  mhos, that of the metal  $5.05 \times 10^6$  mhos. <sup>2</sup>

The transport number of the anion has been investigated by the method of concentration cells. The E.M.F. of these at concentrations from 0.010 to 0.870 shows an enormous increase in the velocity of the negative carrier, which probably consists to a greater and greater extent of electrons, the conductivity at high concentrations being due to the dissociation:



In more dilute solutions some anide may be formed, which then dissociates into ions which have velocities of the usual order <sup>1</sup>:



#### AMMONIA IN AQUEOUS SOLUTION.

**General Properties of Aqueous Solutions.**—Ammonia is easily soluble in water, with evolution of heat. The densities of the solutions are less than that of water. The solution saturated at 15° C. has a density of 0.882 (see table, p. 86). Solutions saturated with the gas at 1 atmosphere contain per gram of water 0.875 grams at 0° C., 0.536 grams at 15° C., and 0.526 grams at 20° C. One volume of water dissolves at 0° C. about 1150 vols. (at N.T.P.), at 20° C. 739 vols. (at N.P.). At lower temperatures the solubilities are greatly increased. The following weights are absorbed by 1 gram of water in equilibrium with ammonia pressures of 743 to 744.5 mm.:—

Temperature, ° C.	= -3.9	-10	-20	-25	-30	-40 <sup>3</sup>
Grams of NH <sub>3</sub>	= 0.947	1.145	1.768	2.554	2.781	2.946

**Ammonia Pressures and Concentrations of Aqueous Solutions.**—Up to normal concentrations and the corresponding ammonia pressures, the gas dissolves nearly according to Henry's Law. <sup>4</sup>

p (in mm. of mercury)	= 5.97	6.71	9.35	13.45
w (grams per litre)	= 7.752	8.602	11.93	17.00
N (mols. per litre)	= 0.456	0.506	0.702	1.00
p/N	= 13.1	13.2	13.3	13.45

That the law does not hold for higher pressures is evident from the tables given below. <sup>5</sup>

<sup>1</sup> All these data refer to a temperature at or near the boiling-point of NH<sub>3</sub>, —33.5° C.

<sup>2</sup> Kraus and Lucasse, *J. Amer. Chem. Soc.*, 1921, 43, 2529.

<sup>3</sup> Mallet, *Amer. Chem. J.*, 1897, 19, 804.

<sup>4</sup> Gaus, Abegg, and Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, 40, 84.

<sup>5</sup> Sander, *ibid.*, 1912, 78, 513.

The relations between  $p$  and  $N$  have been expressed as an interpolation formula <sup>1</sup>

$$p = 13.34N + 0.18N^2.$$

The addition of salts to solutions of ammonia generally raises the ammonia pressure, or diminishes the solubility at a given pressure. The lithium halides are an exception to this rule and increase the solubility of ammonia. Some typical solubilities are given in the table, in which " $p$ " denotes the ammonia pressures (mm.) in equilibrium with various concentrations of the salt in solutions which are normal with respect to total ammonia, and  $\Delta p$  the differences between the pressures of ammonia, *i.e.* 13.45 mm. in equilibrium with a normal aqueous solution, and those in equilibrium with the salt solutions normal in respect to ammonia. <sup>2, 3</sup>

### AMMONIA PRESSURES OF AMMONIACAL SALT SOLUTIONS.

Salt.	Concentration of Salt.					
	0.5 Normal.		1.0 Normal.		1.5 Normal.	
	$p$ .	$\Delta p$ .	$p$ .	$\Delta p$ .	$p$ .	$\Delta p$ .
KCl	14.49	1.04	15.53	2.08	16.63	3.18
$\frac{1}{2}\text{K}_2\text{SO}_4$	15.37	1.92	17.42	3.97	19.85	6.40
$\text{CH}_3\text{—COOK}$	15.55	2.10	17.59	4.14	19.67	6.22
LiI	13.05	—0.40	12.28	—1.17	11.27	—2.18
NaOH	15.37	1.92	17.09	3.64	18.80	5.35

In the case of more concentrated solutions, the comprehensive results of Perman are available. <sup>4</sup> The total pressures of ammonia and water-vapour in equilibrium with solutions of various concentrations and at various temperatures were measured by the static method, *i.e.* on a manometer. Table A is based on these results. In another series, the partial pressures of ammonia and of water-vapour (mm.) in equilibrium with the solutions were determined by the dynamic method, *i.e.* by passing a known volume of air through the solutions, and then through (a) standard dilute and (b) concentrated sulphuric acid. The total increase in the weights of (a) and (b) gives the ammonia plus water, and the decrease in the titre of the sulphuric acid gives the ammonia. Table B is based on these results. By means of this series it was proved that the lowering of the vapour pressures of water in the presence of ammonia is a rectilinear function of the compositions up to 10 per cent. solutions,

$$p_1 = p(1 - x) \text{ ("} p \text{" in mm.)},$$

<sup>1</sup> Locke and Forssall, *Amer. Chem. J.*, 1904, 31, 268.

<sup>2</sup> Callingaert and Huggins, *J. Amer. Chem. Soc.*, 1923, 45, 915.

<sup>3</sup> Gaus, Abegg, and Riesenfeld, *loc. cit.*

<sup>4</sup> Perman, *Trans. Chem. Soc.*, 1901, 79, 718; 1903, 83, 1168.

TABLE A.

## VAPOUR PRESSURES OF AQUEOUS AMMONIA.

(Total pressures, ( $\text{H}_2\text{O} + \text{NH}_3$ ) in mm. of mercury.)

Temperature, ° C.	Percentage of $\text{NH}_3$ .					
	0.	5.	10.	15.	20.	30.
0	4.5	20	35	57	93	220
4	6	21	39	66	110	266
10	9	27	54	89	144	346
14	12	33.5	67	110.5	176	412
20	17.5	47.5	93	151	237	537
30	31.5	83	153.5	245	373	817
40	55	134.5	241	377.5	569.5	1189
50	92.5	210	363.5	564	834.5	..
60	149.5	327	539	816.5	..	..

TABLE B.

## VAPOUR PRESSURES OF AMMONIA AND OF WATER OVER AQUEOUS AMMONIA.

Temperature, ° C.	Percentage of $\text{NH}_3$ .	Pressure of $\text{NH}_3$ (mm.).	Pressure of $\text{H}_2\text{O}$ (mm.).
0	4.72	11.4	5.1
	9.15	24.8	5.3
	14.73	51.3	4.1
	22.90	116.6	2.8
10	4.16	16.5	9.1
	8.26	37.2	8.8
	15.88	95.1	7.0
	21.83	169.8	5.5
19.9	4.18	27.4	16.4
	10.15	80.6	15.1
	23.37	302.4	10.3
30.09	7.43	86.3	29.2
	21.47	404.6	22.1
40.0	7.36	133.0	50.7
	20.85	576.1	37.8
50.0	14.94	487.1	75.2
60.0	11.31	475.8	180.4

in which  $p_1$  are the partial pressures of water over the solutions,  $p$  are the pressures of pure water at the same temperatures, and  $x$  is the fractional amount of ammonia in 1 gram of the solution.

The fact that Raoult's Law is obeyed shows that the molar weight of ammonia as determined by osmotic pressure or depression of the freezing-point is normal at these concentrations. Therefore there is only 1 molecule of ammonia present in the hydrates (*cf.* freezing-point data, p. 87).

The vapour pressures of more concentrated solutions are best expressed by formulæ which are used for binary mixtures of liquids. Thus the pressure-composition isothermals agree with the Margules equation

$$\frac{d \log p_1}{d \log x_1} = \frac{d \log p_2}{d \log (1-x_1)}$$

in which  $p_1$  and  $x_1$  refer to the ammonia, and  $p_2$  and  $1-x_1$  to the water. Thus for  $x=0.2088$  (20.88 per cent.  $\text{NH}_3$  at  $20^\circ \text{C.}$ ),  $p_1=228.5$ ,  $dp_1=13$ ,  $dp_2=0.825$ :

$$\frac{p_1(1-x)}{p_2x} = 66.6 \qquad \frac{dp_1}{dp_2} = 61.8.$$

Table A gives the total pressures of solutions containing from 0 to 30 per cent. of ammonia between  $0^\circ$  and  $62^\circ \text{C.}$  The pressures were measured by the static method, *i.e.* on a manometer connected with the space above the solutions, which were kept at the controlled temperatures by the vapours of various liquids boiling at atmospheric pressure.<sup>1</sup>

At  $100^\circ \text{C.}$  the following ratios between the concentrations,  $C_1$ , of ammonia in the gas phase, and those,  $C_2$ , in solution, increase with increasing concentration, but the ratios  $K = \frac{C_1}{C(1-a)}$ , in which  $C(1-a)$  is the "ion residue," or total ammonia not present as ions, is nearly constant.

$C = 1.256$	0.633	0.305	0.148	0.0386	0.0190	0.0107	0.0046
$\frac{C_1}{C} = 12.92$	12.67	12.44	12.13	12.06	11.83	11.53	11.05
$K = 13.1$	12.9	12.8	12.6	13.0	13.2	13.3	13.6

Table B gives the experimental partial pressures of ammonia and water-vapour in equilibrium with solutions. The pressures were determined by the dynamic method already described. The total pressures found as the sums of those of the ammonia and water by the dynamic (air current) method usually agree within 1 per cent. with the corresponding pressures found by the static (manometer) method, although in a few cases there is a discrepancy of 2 to 3 per cent. These results have also been in a table which gives values at intervals of  $2^\circ \text{C.}$  from 0 to  $60^\circ$ .<sup>2</sup>

The partial pressures of ammonia and of water in equilibrium with the concentrated solutions have been redetermined with the aid of elaborate apparatus by Neuhausen and Patrick.<sup>3</sup> The dynamic method outlined above was criticised on grounds which were indeed noted by Perman.<sup>4</sup>

<sup>1</sup> Perman, *Trans. Chem. Soc.*, 1901, 79, 718; 1903, 83, 1168.

<sup>2</sup> Perman, *ibid.*, 1903, 83, 1174.

<sup>3</sup> Neuhausen and Patrick, *J. Physical Chem.*, 1921, 25, 693.

<sup>4</sup> His results include more dilute solutions, and also show how much ammonia is actually evaporated under the conditions stated.



The static method employed gives accurately the vapour pressure of the water, which is the minor constituent in the case of these solutions. The pressure of pure ammonia gas, admitted into one tank from the reservoir of liquid, was measured against that of a similar tank containing ammonia plus water-vapour on a differential manometer with an obtuse angle of  $157^\circ$  (i.e. each limb  $11.5^\circ$  to the horizontal). Water-vapour was injected into the second tank until the pressure, which rises at first (because the volume is constant), reaches a maximum, and then falls as solution is condensed, carrying with it some of the ammonia in the dissolved state. The results are given in Table C ( $t=20^\circ$  and  $40^\circ$  C.). Those due to Berthoud<sup>1</sup> are given in Table D ( $t=0^\circ$  C.).

TABLE C.

**PARTIAL PRESSURES OF AMMONIA AND OF WATER, DENSITIES AND CONTRACTIONS OF AQUEOUS AMMONIA.<sup>2</sup>**

( $p$  in mm. of mercury.)

Temperature, ° C.	Molecular Per- centage of $\text{NH}_3$ .	$p_{\text{NH}_3}$ .	$p_{\text{H}_2\text{O}}$ .	Density.	Percentage Contraction.
20	34.886	728	9.4	0.882	7.07
	43.731	1281	8.3	0.848	7.37
	56.923	3277	4.15	0.815	9.65
40	25.011	752	36.5	0.902	6.05
	36.126	1787	23.9	0.864	8.22
	46.335	3640	17.6	0.828	9.40
0	51.676	915	1.25	0.842	7.50
	61.206	1409	0.77	0.817	9.21
	66.621	1865	0.46	0.795	8.12

The densities of aqueous ammonia solutions at  $15^\circ$  C. are given in the well-known tables of Lunge and Wiernik,<sup>3</sup> and have been redetermined by Price and Hawkins.<sup>4</sup> A selection of comparative values from both sets of observations is given in Table D.

**Hydrates of Ammonia.**—The freezing-point curve for aqueous solutions of ammonia indicates the existence of two hydrates and three eutectic mixtures.<sup>5, 6, 7, 8</sup> The following data are due to Rupert; those in brackets to Smits and Postma:—

<sup>1</sup> Berthoud, *Helv. Chim. Acta*, 1918, 1, 84.

<sup>2</sup> The figures "x" in the second column can be converted into grams per cent. "p" by the formula

$$p = \frac{17.03 x}{1801.6 - 0.984 x}$$

The contractions in the fifth column (at  $0^\circ$ ) are calculated as the differences between the sum of the volumes of liquid ammonia and water and the volume of the solution.

<sup>3</sup> Lunge and Wiernik, *Zeitsch. angew. Chem.*, 1889, 2, 181.

<sup>4</sup> Price and Hawkins, *J. Soc. Chem. Ind.*, 1924, 43, 113T.

<sup>5</sup> Baud and Gay, *Compt. rend.*, 1909, 148, 1327.

<sup>6</sup> Rupert, *J. Amer. Chem. Soc.*, 1909, 31, 866; 1910, 32, 748.

<sup>7</sup> Smits and Postma, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 186; 1914, 17, 182.

<sup>8</sup> Postma, *Rec. Trav. chim.*, 1920, 39, 515.

<i>Hydrates</i>		$2\text{NH}_3\cdot\text{H}_2\text{O}$	$\text{NH}_3\cdot\text{H}_2\text{O}$
Molecular percentage of $\text{NH}_3$ in the solution		65.40	48.59
Freezing-point, ° C.		-79 (-78.8)	-79 (-79)
<i>Eutectic mixtures</i> ---			
Solid phases	$\text{NH}_3$ and $2\text{NH}_3\cdot\text{H}_2\text{O}$	$2\text{NH}_3\cdot\text{H}_2\text{O}$ and $\text{NH}_3\cdot\text{H}_2\text{O}$	$\text{NH}_3\cdot\text{H}_2\text{O}$ and $\text{H}_2\text{O}$
Molecular percentage of $\text{NH}_3$ in solution	78.5 (81.4)	57.5 (58.5)	32 (34.7)
Freezing-point, ° C.	-96 (-92.5)	-86.5 (-86)	-115 (-100.3)

The *monohydrate* forms small colourless crystals and the *hemihydrate* larger transparent needles. Solutions containing about 33 per cent. of ammonia are very viscous at  $-100^\circ\text{C}$ .

TABLE D.  
DENSITIES OF AQUEOUS AMMONIA.

Density.	Percentage of $\text{NH}_3$ . (P. and H.)	Percentage of $\text{NH}_3$ . (L. and W.)	Density.	Percentage of $\text{NH}_3$ . (P. and H.)	Percentage of $\text{NH}_3$ . (L. and W.)
0.875	36.90		0.950	12.74	12.71
880	35.20	35.51	960	9.95	9.88
890	31.85	31.65	970	7.27	7.29
900	28.50	28.25	980	4.73	4.79
910	25.15	24.92	990	2.31	2.30
920	21.85	21.70	920	1.84	1.83
930	18.69	18.60	940	0.91	0.91
940	15.65	15.59	960	0.45	0.45

#### AMMONIA IN SOLUTION IN SOLVENTS OTHER THAN WATER.

The solubilities of ammonia in the lower aliphatic alcohols are considerable, although lower than those in water. Thus methyl alcohol dissolves 40 per cent. of ammonia at  $0^\circ\text{C}$ . The solubilities (under corresponding conditions of temperature and ammonia pressure) diminish with increasing molecular weight of the alcohol; in ethyl alcohol the solubilities are:

Temperature, ° C.	0	20
Solubility in grams of $\text{NH}_3$ per litre of alcohol	130.5	75
Density of solution	0.782	0.791

These solubilities are increased on the addition of water.<sup>1</sup> Comparative solubilities of ammonia in ethyl, isopropyl, and isobutyl alcohols have also been determined at  $t^\circ = 20^\circ \pm 0.4^\circ\text{C}$ .<sup>2</sup>

<sup>1</sup> Delepine, *J. Pharm.*, 1892, [5], 25, 496.

<sup>2</sup> Pagliano and Erno, *Atti Acc. Torino*, 1882, 18, 67.

Alcohol.	Ethyl.	Isopropyl.	Isobutyl.
Ammonia pressure in mm. of mercury	457	456.6	523.1
Solubility, as volumes of ammonia gas dissolved by one volume of alcohol .	70.9	56.6	59.1

The following results show a diminution in the heat of solution of ammonia as the molar weight of the alcohol increases <sup>1</sup> :—

Alcohol.	Methyl.	Ethyl.
Range of concentration as percentage of NH <sub>3</sub> . . . . .	0.17 to 9.94	0.30 to 4.23
Heat of solution in calories per mol. of NH <sub>3</sub> . . . . .	818 to 1508	703 to 1230

The ratio in which ammonia is distributed between water and toluene is 26 at 19.5° C., and decreases with increasing concentration.<sup>2</sup>

The distribution ratio between water and chloroform <sup>2</sup> was redetermined by Moore and Winnill,<sup>3</sup> who found 24.25 at 25° C. over the range of concentrations given in the table. The ratio alters considerably at higher concentrations according to Bell and Field.<sup>4</sup> They find 24 in dilute solution, rising to 10 in very concentrated solution. Since this ratio is scarcely affected by the presence of ammonium chloride, the variation cannot be accounted for by a variation in the ionic equilibrium. It must be referred to the effect of increasing concentration on the relative proportions of the dissolved and hydrated ammonia molecules (*vide infra*, p. 92).

### DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM.<sup>5</sup>

Temperature, ° C.	Concentration of NH <sub>3</sub> in Water, C <sub>1</sub> , as Mols. per Litre.	Distribution Ratio Water/Chloroform, $\frac{C_1}{C_2}$	Authority.
18	0.07709 0.11989	27.42 27.44	Moore and Winnill. <sup>3</sup>
	0.154	26.01	
19.5	0.336 0.1498	25.67 24.43	Dawson and McCrae. <sup>2</sup>
	0.169	24.25	
25	0.1987	24.26	Moore and Winnill.
	0.0999	21.20	
32.35	0.2420	21.17	

<sup>1</sup> Timofejew and Brylik, *Chem. Zentr.*, 1905, ii, 431.

<sup>2</sup> Dawson and McCrae, *Trans. Chem. Soc.*, 1906, 89, 1666.

<sup>3</sup> Moore and Winnill, *ibid.*, 1912, xix, ii, 1667. See also Hautzsch and Sebaldt, *Zeitsch. physikal. Chem.*, 1899, 38, 258.

<sup>4</sup> Bell and Field, *J. Amer. Chem. Soc.*, 1911, 33, 940.

<sup>5</sup> Only the experimental concentrations, C<sub>1</sub>, of the ammonia in the aqueous layer are given. From these, the concentrations in the chloroformic layers can be obtained after division by the ratios  $\frac{C_1}{C_2}$ .

Since it is probable that ammonia dissolves in organic solvents of the water immiscible type as simple molecules, the distribution ratio between such solvents and water should give information as to the concentrations of simple molecules present in aqueous solution. This principle has been extensively used, *e.g.* to determine the hydrolytic equilibria of ammonium salts.

**Conductivity and Dissociation Constant.**—The weakly alkaline reactions of solutions which contain dissolved ammonia are due to a slight electrolytic dissociation into NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions. The approximate degrees of dissociation derived from the conductivities in the usual manner are :

Normality of solution	.	.	0.01	0.10	1.0
Percentage dissociation	.	.	4	1	0.3

The maximum conductivity is attained at a normality of about 3, at which  $\kappa \times 10^4$  (see below) = 11 (at 18° C.) and 13 (at 25° C.), and then falls to 1.93 in a 16 times normal solution (at 18° C.) and to 4.3 in a 13 times normal solution (at 25° C.). In the tables, the values of the conductivities at 18° C. are due to Kohlrausch,<sup>1</sup> those at 25° C. to Goldschmidt,<sup>2</sup> with the exception of the first two at the lowest concentrations, which are due to Bredig.<sup>3</sup>

### CONDUCTIVITIES OF AQUEOUS AMMONIA SOLUTIONS.

TABLE A (AT 18° C.).<sup>1</sup>

C in mols. per litre =	0.059	0.234	0.467	0.933	2.307	4.55	8.87	16.01
$\kappa \times 10^4$ =	2.51	4.92	6.57	8.67	10.95	10.38	6.32	1.93

TABLE B (AT 25° C.).<sup>2, 3</sup>

C	0.0039	0.0078	0.0109	0.0219	0.0553	0.1107	0.3148	0.541	0.666	0.817
$\kappa \times 10^4$	0.741	1.046	1.220	1.730	2.718	3.843	6.339	7.882	8.776	9.510
C	0.953	1.081	1.586	2.190	2.955	3.521	4.720	7.930	9.204	12.89
$\kappa \times 10^4$	10.02	10.57	11.77	12.70	12.96	12.91	12.18	8.703	7.910	4.323

The mobility of the ammonium ion, L<sub>0</sub>, at zero concentration has been determined as follows :—

Temperature, ° C. =	18	25	32.85
L <sub>0</sub> =	64 <sup>1</sup>	70.4 <sup>3</sup>	84.9 <sup>4</sup>
L <sub>0</sub> =	63.7 <sup>4</sup>	74.4 <sup>4</sup>	

The molar conductivities at zero concentration,  $\lambda_0$ , that is, the sums of the ionic conductivities of the ammonium and hydroxyl ion at zero (the lowest limiting) concentration, are as follows :—

<sup>1</sup> Kohlrausch, *Wied. Annalen*, 1879, [6], i, 145.

<sup>2</sup> Goldschmidt, *Zeitsch. anorg. Chem.*, 1901, 28, 97.

<sup>3</sup> Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 289.

<sup>4</sup> Moore and Winmill, *Trans. Chem. Soc.*, 1912, 101, ii, 1667.

Temperature, ° C.	=	18	25
$\lambda_0$	=	237.7	270.3

Ammonia is a weak or "half" electrolyte, the ionisation of which obeys the dilution law. Putting in the values of  $\alpha = \frac{\lambda}{\lambda_0}$  derived from the conductivities into the equations

$$\frac{\alpha^2 C}{1-\alpha} \quad \text{or} \quad \frac{\alpha^2}{(1-\alpha)V} = k,$$

a constant is obtained which is found to hold good for the more dilute solutions. It must be carefully noted that the "undissociated ammonia,"  $1-\alpha$ , includes all forms not present as ions. The constant " $k$ " is therefore an apparent one. It has the greatest practical utility, as it is available for calculating the alkalinities of ammonia solutions, as well as the acidities and degrees of hydrolysis of ammonium salts. The value of the constant of basic dissociation into ammonium and hydroxyl ions,  $k_B$  at about 18° C., is  $1.7$  to  $1.8 \times 10^{-5}$ . From the determination of  $\lambda$  and  $\lambda_0$  at other temperatures the following values of the constant are obtained :—

Temperature, ° C.	=	0	18	25	32.35	50
$10^5 k$	=	1.39 <sup>1</sup>	1.72 <sup>2</sup>	1.80 <sup>1,2</sup>	1.887 <sup>2</sup>	1.81 <sup>1</sup>

At higher temperatures the constant diminishes ; thus  $10^5 k$  is 1.35 at 100° C. and 0.0093 at 306° C.<sup>3</sup>

The apparent constant also holds good, not only for free ammonia and its salts, but also for partly neutralised solutions of ammonia, so that from it the acidities " $h$ " (or alkalinities) of any given mixture can be calculated by means of the equation

$$[H] = \frac{k_w \times \text{concentration of added acid}}{k_B \times \text{concentration of free ammonia}}$$

( $k_w$  is the water constant =  $1 \times 10^{-14}$  at 23° C.).

The acidities of solutions of ammonium salts may be calculated from the equation

$$[H] = \sqrt{\frac{k_w C}{k_B}},$$

when  $k_B = 1.8 \times 10^{-5}$ .

At C. (normality)	=	1.0	0.1	0.01
$p_H (= -\log [H])$	=	4.62	5.12	5.6

These acidities correspond well with the turning-point of methyl red, and consequently this is a good indicator for the accurate titration of ammonia.

The converse calculation, that of the ionisation constants from the hydrolysis of ammonium salts, has been made by Lunden :<sup>4</sup>

At t° C.	=	0	18	25	40	60
$10^5 k$	=	1.4	1.77	1.87	1.98	1.9

<sup>1</sup> Kangt, *J. Amer. Chem. Soc.*, 1907, **29**, 1414.

<sup>2</sup> Moore and Winmill, *Trans. Chem. Soc.*, 1912, **101**, ii, 1667.

<sup>3</sup> Noyes, Kato, and Sosman, *Zeitsch. physikal. Chem.*, 1910, **73**, 20.

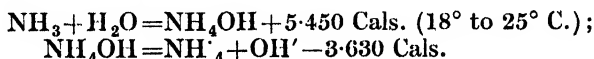
<sup>4</sup> Lunden, *J. Chim. phys.*, 1907, **5**, 574.

**Thermochemistry and Thermodynamics of Ammonia Solutions.**—The total (or integral) heat of solution of ammonia in water as determined by calorimetric methods is 8·430 Cals. for 1 mol. of ammonia in 200 mols. of water.<sup>1</sup> The differential heat of solution (1 mol. in a large quantity of a solution having any given concentration) is also positive. It may be calculated by the Clapeyron equation from the ammonia pressures of, e.g., a dilute solution as above at 10° and 30° C., and is found to be 8·700 Cals. per mol. at 20°.² This heat may be divided into (a) the latent heat of condensation of ammonia to the liquid form; (b) the heat of solution, hydration, ionisation.

(a) The latent heat of condensation to liquid is 5·000 Cals. in round numbers.<sup>3</sup> From the vapour pressures, the latent heats at various temperatures have been calculated and expressed by the formula

$$L = 32\cdot968\sqrt{133-t} - 0\cdot5895(133-t).^4$$

This gives a molar latent heat of 4·890 Cals. at 15°. The differentiation of one formula of Cragoe, Meyers, and Taylor gives 3·950 Cals. Then approximately 8·430—5·000=3·430 Cals. are evolved in solution, hydration, and ionisation when liquid ammonia is dissolved in dilute solution. The heat of ionisation,  $Q_i$ , is determined from the change in the dissociation constant with the temperature. Thus the mean value of  $Q_i$  between 18° and 25° is -1·190 Cals. (Moore and Winnill's results, *loc. cit.*), while between 0° and 25° it is -1·675 (Kanolt's results). See Lunden.<sup>5,6</sup> The heat of ionic dissociation is also obtained as the difference between the heats of neutralisation of (a) ammonia,  $Q_1$ , and (b) a strong base,  $Q$ , with a strong acid; thus  $Q_i = Q_1 - Q = 12\cdot300 - 13\cdot800 = -1\cdot500$  Cals. ( $Q_1$  is 12·300 Cals. in the case of 0·278N ammonia, according to Thomsen.<sup>1</sup>) From the results of distribution experiments between water and chloroform, and of conductivity determinations, the following heats may be deduced:—<sup>7</sup>



Hence, allowing for the proportions present in the solution, of NH<sub>3</sub>, NH<sub>3</sub>·xH<sub>2</sub>O and ammonium hydroxide (or any other kind of molecule which is in direct equilibrium with the ions), it is calculated that the

<sup>1</sup> Thomsen, *Thermochemistry*, transl. by Burke (Longmans, 1908).

<sup>2</sup> Perman, *Trans. Chem. Soc.*, 1901, 79, 718.

<sup>3</sup> Strombeck, *J. Frank. Inst.*, 1891, 131; Dieterici, *Zeitsch. Kalleind.*, 1904, p. 1.

<sup>4</sup> Osborne and van Dusen, *J. Amer. Chem. Soc.*, 1918, 40, 1.

<sup>5</sup> Lunden, *Ahren's Sammlung*, 1909, 14, 65.

<sup>6</sup> The apparent heat of dissociation,  $Q_i$  (calculated from the apparent constant  $k_B$  of ammonia), is equal to the sum of the true heat,  $Q'_i$  (calculated from the true dissociation constant  $k$ ), and the heat of hydration of dissolved ammonia (called  $\text{NH}_3$ ).

$$\begin{array}{lll}\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4' + \text{OH}' & k_1 u = i^2 & \frac{d \log k_1}{dt} = \frac{-Q'_i}{RT^2} \\ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} & k_2(\text{NH}_3) = u & \frac{d \log k_2}{dt} = \frac{-Q_2}{RT^2} \\ k_B(u + [\text{NH}_3]) = i^2 & \frac{d \log k_B}{dt} = \frac{-Q_i}{RT^2} & Q_i = Q'_i + \frac{1}{1 + k_2} Q_2\end{array}$$

In which "i" stands for ions, "u" for undissociated part.

<sup>7</sup> Moore and Winnill, *loc. cit.*

heat of neutralisation in a 0.278N solution at 18° C. is 12.320 Cals., agreeing well with the value of Thomsen.

**The Molecules present in Aqueous Ammonia.**—In the foregoing account of the solubility, dissociation, and thermochemistry of ammonia solutions, a judgment as to the kind of molecule which is produced by the hydration was left in suspense as far as possible. It is, however, convenient to use the term *hydrate* for that part of the ammonia which is in direct equilibrium with the gas, and the term *hydroxide* for that which is in equilibrium with the ions. The presence of one or more hydrates which may be more or less dissociated into  $\text{NH}_3$  and  $\text{H}_2\text{O}$  is probable, and the presence of the ion  $\text{NH}_4^+$  in low concentration and perhaps also hydrated is demonstrated by electrochemical evidence. But whether an "ammonium hydroxide" analogous to sodium hydroxide exists in solution is open to doubt. It has been pointed out by Caven,<sup>1</sup> that, according to the present electronic theory of valency, the ammonium ion is formed by the direct addition of the hydron of water to  $\text{NH}_3$ , and that the assumption of a non-ionised intermediate ammonium hydroxide is unnecessary. On the other hand, Moore<sup>2</sup> has shown that the distribution ratios between water and chloroform, taken along with the electrolytic dissociation equilibria, require (that is, if the law of concentration action is assumed) a considerable proportion of ammonium hydroxide; so that the true dissociation constant  $k'$  is not the same as the apparent constant  $k_B$ .<sup>3</sup> The following table gives the values of the various molecular species calculated from these results. The constant  $k_B$  is  $1.725 \times 10^{-5}$  (at 18° C.):—

### THE MOLECULES PRESENT IN AQUEOUS AMMONIA.

(Concentrations in mols. per c.c.,  $\times 10^5$ .)

Temp., ° C.	Total $\text{NH}_3$ in any Form.	$\text{NH}_3 \cdot x\text{H}_2\text{O}$ . Hydrated Ammonia.	$\text{NH}_4\text{OH}$ . Ammonium Hydroxide.	$\text{NH}_4^+$ . Ammonium Ion.	$k_2 \times 10^6$ . Hydration Constant.	$k'_B \times 10^5$ . Dissociation Constant.
18	11.99	4.92	6.92	0.143	1.41	2.94
25	14.98	6.97	7.85	0.164	1.13	3.41
32.35	9.99	5.31	4.53	0.136	0.85	4.11

The different views may be reconciled in various ways. The hydron may attach itself to the  $\text{NH}_4^+$  which is already hydrated, giving the hydrated ion  $x\text{H}_2\text{O} \cdot \text{NH}_4^+$ . On this hypothesis,  $\text{NH}_3 \cdot x\text{H}_2\text{O}$  in the above table may be substituted for  $\text{NH}_4\text{OH}$  without affecting the quantitative relations; while for  $\text{NH}_3 \cdot x\text{H}_2\text{O}$  there would be substituted  $\text{NH}_3$  dissolved as such. It seems probable on the electronic theory that non-ionised  $\text{NaOH}$ , like non-ionised  $\text{NaCl}$ , does not exist, only the ions being present at all dilutions, because the electron has already passed from all the Na on combination. Only a portion of these

<sup>1</sup> Caven, *J. Soc. Chem. Ind.*, 1923, 42, 165.

<sup>2</sup> Moore, *Trans. Chem. Soc.*, 1907, 91, 1373; Moore and Winmill, *ibid.*, 1912, 101, 1667.

<sup>3</sup> See p. 91, note 6.

ions, however, *i.e.* those which conduct the current, are dissociated. In the same sense we may suppose that non-ionised  $\text{NH}_4\text{OH}$  does not exist; the  $\text{NH}_3$  which has attached a hydrogen ion is a positive ion at all dilutions. But a part of this is not dissociated, and takes the place of the older non-electrolyte, ammonium hydroxide, in calculations involving ammonium and hydroxyl-ion concentrations.

#### DETECTION AND ESTIMATION.

**Detection.**—Moderate quantities in the air or in solution are recognised by the smell, by the brown colour imparted to yellow turmeric, by the blue to red or purple litmus, and generally the alkaline colour to indicators of the "weak alkali sensitive" class, such as Congo blue or methyl orange. The latter, however, are rather too sensitive, as they change in time when exposed to ordinary air. The blackening of mercurous nitrate is also a good test. All these indicators are best applied in the form of test papers.

Traces of ammonia and its salts in solution are recognised by means of Nessler's solution (see p. 94). If sulphides are present, they also impart a dark colour to Nessler's solution; but this persists on the addition of acids, whereas the brown due to ammonia is destroyed by acids.

**Estimation.**—Free ammonia in solution is usually estimated by titration with standard acid.

Since the ammonia is continually being lost in the vapour, the solutions should be diluted and kept in a well-stoppered bottle or titrated at once, or treated with an excess of standard acid.

On account of the hydrolysis of solutions of ammonium salts, which therefore react acid (see p. 90), the end point of the titration is found with an "acid-insensitive" or "alkali-sensitive" indicator such as methyl orange, or better, methyl red.

The ammonia in ammonium salts may be determined after distillation with alkali and absorption of standard acid. A weighed amount of the salt is dissolved in boiled water treated with excess of 10 per cent. boiled sodium-hydroxide solution and distilled from a flask provided with a "spray trap" or "splash bulb." Many forms of apparatus are described in the text-books of analytical chemistry. The distillate is taken up, or the evolved gases pass through, a known excess of standard, usually 0.5N acid, and the excess titrated back with standard alkali as described above.

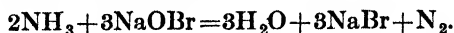
If the ammonia is present as the salt of a volatile acid (*e.g.* as carbonate), it may be boiled with standard sulphuric acid, and the excess of this titrated as above. In the determination of nitrogen in organic compounds by the Kjeldahl method, the nitrogen is finally obtained as ammonium sulphate dissolved in concentrated sulphuric acid. This is distilled with an excess of alkali, etc., in the manner already described. If the quantities of ammonia are small, they may be condensed with water and determined by the Nessler method (see p. 94).

Ammonium salts may also be estimated quickly, although less accurately, by loss.<sup>1</sup> The salt (*e.g.* 10 grams) is dissolved in water, treated with an excess of alkali, and made up to a known volume, *e.g.* of 1 litre.

<sup>1</sup> Jean, *Ann. Chim. anal.*, 1904, 9, 257.



A measured volume of this, *e.g.* 25 c.c., is titrated directly, using methyl red (*a*). Another 25 c.c. is diluted, boiled in a flask until the steam is free from ammonia, and then titrated (*b*). The difference between the titrations (*a*)—(*b*) gives the ammonia. A gas volumetric method is also available, which depends upon the decomposition by sodium hypobromite, with evolution of nitrogen :<sup>1</sup>



The alkaline hypobromite is run into the solution of ammonium salt in a nitrometer and the volume of nitrogen measured and corrected to N.T.P. in the usual manner. Since the decomposition is not quite complete (owing to the existence of a little ammonium hypobromite) a blank analysis is carried out on a standard solution of ammonium salt, and a correction factor is thus evaluated.

Ammonia may be estimated gravimetrically after precipitation by chloroplatinic acid. The precipitate may be dried at 130° and weighed as  $(\text{NH}_4)_2\text{PtCl}_6$ , or ignited to platinum.

Ammonia present as salts may be indirectly estimated by Ronchese's method.<sup>2</sup> Formaldehyde converts the ammonia into hexamethylene tetramine (hexamine, urotropin), and the liberated acid is titrated in the presence of phenolphthalein :



Any free acid originally present is first neutralised, the amount of alkali necessary being determined by a preliminary titration in the presence of methyl orange or methyl red. Formalin containing 20 per cent. of formaldehyde, previously neutralised if necessary to phenolphthalein, is added in slight excess. The titration is then carried out in the usual manner with standard acid. The method is not applicable to the ammonium salts of weak acids.<sup>3</sup>

Small quantities of ammonia, free or combined as salts, are estimated colorimetrically with the aid of Nessler's solution, potassium mercuric iodide,  $\text{K}_2\text{HgI}_4$ , with an excess of sodium or potassium hydroxide. The brown precipitate, or brown or yellow colour, is the compound  $\text{O}-\text{Hg}_2-\text{NH}_2-\text{I}$ , which has great colouring power.

The solution to be tested is made alkaline with sodium hydroxide and carbonate, allowed to stand until any carbonates of calcium magnesium or iron settle, and a measured portion of the clear solution is tested with 1 c.c. or more of the Nessler reagent. If the amounts of ammonia are small, as usually in waters, 100 or 200 c.c. are treated with sodium carbonate or a suspension of magnesium carbonate (both of which must of course be free from ammonia) and distilled from a flask through a Liebig's condenser. Successive portions of the distillate are treated with 2 c.c. of the Nessler reagent, and the yellow or brown colours are matched against that produced by a very dilute standard solution of ammonium chloride. The well-known cylindrical Nessler glasses of colourless glass, holding 50 or 100 c.c., are used for the comparison. 0.01 mgm. of ammonia can easily be determined by this method.

<sup>1</sup> Knop, *Centralblatt*, 1860, p. 243; Wagner, *Zeitsch. anal. Chem.*, 1876, 15, 250.

<sup>2</sup> Ronchese, *J. Pharm. Chim.*, 1907, (vi), 25, 611.

<sup>3</sup> Wilkie, *J. Soc. Chem. Ind.*, 1910, 29, 6. See also Gaillot, *Ann. Chim. anal.*, 1913, 18, 15.

THE REACTION  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ .

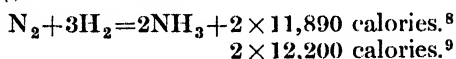
As already mentioned, the passage of electric sparks, which effects an almost complete decomposition of preformed ammonia, also causes the gases to combine to a small, but definite, extent. The same is true of catalytic agents, such as finely divided iron, which accelerate not only the decomposition, but also the formation of ammonia and lead to a true equilibrium. This equilibrium may be set up at ordinary temperatures in the presence of platinum black or colloidal noble metals, when the mixture of gases is passed through acidulated water at 90° C., containing these catalysts. Or hydrogen may be passed through solutions from which nitrogen is being evolved.<sup>1</sup>

It has long been known that nitrogen and hydrogen will combine in the presence of suitable catalysts, and it was suggested by Clark in 1874, that ammonia might be made by passing them over chromium, manganese, iron, or cobalt. The systematic investigation of the equilibrium proportions of ammonia formed by relatively low temperature catalysis was taken up by Haber,<sup>2</sup> Perman,<sup>3, 4</sup> and their co-workers from 1904 onwards.

The affinity<sup>5</sup> of the formation of ammonia from its elements is positive. The reversible potential between platinum electrodes traversed by nitrogen and hydrogen respectively, which are immersed in a solution of ammonium nitrate and ammonia, is about 0.6 volts.<sup>6</sup> The decomposition potential of 25 per cent. aqueous ammonia is +0.63 volts.<sup>7</sup> These results indicate that the equilibrium amounts of ammonia which should be formed under reversible conditions at ordinary temperatures should be high.

**Heat of Formation.**—Ammonia is an exothermic compound, and the heat of formation under various conditions has been carefully determined, both directly and also from the alteration of the equilibrium constants, with the temperature.

The heat of formation, as determined thermochemically for ordinary temperatures, is given as follows :—



The heat of formation from its elements at various temperatures has been obtained by the catalytic decomposition of ammonia in a calorimeter.<sup>10</sup> The heat absorbed was just compensated by electrically heating the catalyst so that the temperature remained constant. The electrical energy supplied per second is equal to the heat of formation of that amount of ammonia which is decomposed per second, viz. :

t° C. =	0	466	503	554	659
Heat of formation, Q =	10,950	12,670	12,700	12,900	13,150

<sup>1</sup> Zeughelis, *Compt. rend.*, 1916, 162, 914.

<sup>2</sup> Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1905, 44, 341.

<sup>3</sup> Perman, *Proc. Roy. Soc.*, 1905, 76, [A], 167.

<sup>4</sup> Perman and Atkinson, *ibid.*, 1904, 74, 110.

<sup>5</sup> The affinity in this case has the same sign as the heat of formation.

<sup>6</sup> Baur, *Zeitsch. anorg. Chem.*, 1902, 29, 305.

<sup>7</sup> Frenzel, *ibid.*, 1902, 32, 319.

<sup>8</sup> Thomsen, *Thermochemistry*, transl. by Burke (Longmans, 1908).

<sup>9</sup> Berthelot and Matignon, *Ann. Chim. Phys.*, 1880, [5], 20, 253.

<sup>10</sup> Haber, Tamaru, and Öholm, *Zeitsch. Elektrochem.*, 1915, 21, 191.

Omitting the third value, which is discordant, the heat can be expressed as a function of the temperature by the equation

$$Q = 10,950 + 4.54t - 0.001822t^2 \text{ calories,}$$

or

$$Q = 9,575 + 5.535T - 0.001822T^2 \text{ calories,}$$

10,950 and 9,575 calories being the heats of formation at zero centigrade and zero on the absolute scale respectively.

Another equation proposed is :

$$Q = 9,465 + 5.819T - 0.001261T^2 + 0.00471T^3 \text{ calories.}^1$$

The variation in the heat of the formation with the temperature is also given by the Kirchhoff Law,

$$Q_t - Q_0 = \Sigma nCt,$$

in which  $\Sigma nC$  refers to the molar heats of the reacting gases (positive) and resulting gases (negative), each multiplied by the number of molecules participating in the reaction.

The values of  $C$ , the molar heats, are :

Nitrogen . . .	$6.58 + 0.00053t.$
Hydrogen . . .	$6.8 + 0.0003t.$
Ammonia . . .	$8.62 + 0.00175t + 1.7 \times 10^{-6}t^2.$

In the formation of 1 mol. of ammonia,



Hence

$$\Sigma nC = 4.87 - 0.001035t - 1.7 \times 10^{-6}t^2,$$

and

$$Q = 10,950 + 4.87t - 0.001035t^2 - 1.7 \times 10^{-6}t^3 \text{ calories.}$$

The values of  $Q$ , calculated from this, agree fairly well with those found by thermochemical methods.

The variation in the constants of the reaction, viz.,

$$K_c = \frac{(NH_3)}{(H_2)^{\frac{3}{2}}(N_2)^{\frac{1}{2}}} \quad \text{and} \quad K_p = \frac{p_{NH_3}}{p_{H_2}^{\frac{3}{2}} \times p_{N_2}^{\frac{1}{2}}},$$

and, of course, also of the affinity of the reaction

$$A = RT \log K_c,$$

may be obtained as a function of the heat of reaction and specific heats, by integration of the van 't Hoff isochore :

$$\frac{d \log K_c}{dt} = \frac{-Q_v}{RT^2}.$$

Since  $+Q_v$ , the heat of the reaction at constant volume, is positive, the constant  $K$  must diminish with rising temperature, as is seen by the integrated form :

<sup>1</sup> Shilling, *Trans. Faraday Soc.*, 1926, (vi), 22, 396.

$$\log K_{t_2} - \log K_{t_1} = \frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

Since the right-hand side of the equation is negative ( $T_2$  is greater than  $T_1$ ), there is less ammonia in the equilibrium mixture at the higher temperature. Actually the values of  $K$  determined at each temperature are those at constant pressure  $K_p$ , and

$$\log K_p = \log K_c + \Sigma n \log RT.$$

The  $Q$  values observed are also those at constant pressure, and

$$Q_p = Q_c + \Sigma n \log RT.$$

$Q$  is a function of the temperature (as shown above), and its temperature coefficients must be included in the integration, giving the equation

$$\log_{10} K_p = \frac{2095}{T} - 2.7884 \log_{10} T + 0.0003986T + \text{constant} \quad (1)$$

The integration constant may be evaluated by a determination of the equilibrium at one temperature, or approximately by means of the Nernst heat theorem. By the first method the constant is 2.6253. ( $K_p = 0.000273$  at  $t = 880^\circ \text{C}$ .)

Another equation, used by Haber, is—

$$\log_{10} K_p = \frac{2098}{T} - 2.5088 \log_{10} T - 0.0001006T + 0.186 \times 10^{-6}T^2 + 2.1 \quad (2)$$

A shortened form of this equation,

$$\log_{10} K_p = \frac{2888}{T} - 6.134 \quad (3)$$

is sufficiently accurate for many purposes.<sup>1</sup>

By the use of the equations representing the most probable specific heat of ammonia at each temperature (see p. 96), and also those representing the variation of the equilibrium constant with the temperature (see above), another equation has been obtained, viz. :

$$\log K_p = \frac{2068}{T} - 2.9728 \log T + 0.032756T + 0.07513T^2 + 3.1490 \quad (4)^2$$

which gives results in good agreement with those of Table A.

**The Equilibrium Constants at Different Temperatures.**—The following tables contain the most important of the experimentally determined values of  $K_p$ , which are compared with those calculated by equations (1) and (2).

<sup>1</sup> These formulæ indicate that the heat reaches a maximum at a certain temperature and then diminishes, becoming zero at very high temperatures and then negative. The equilibrium percentage of ammonia should at this point begin to rise again, and the possibility is thus given that ammonia is formed at high temperatures. In support of this deduction there is the fact that ammonia can be synthesised by the spark discharge (Dixon, *Proc. Manch. Lit. Phil. Soc.*, 1888, [4], i, 91). Also the spectrum of ammonia contains a series of lines in the ultra-violet corresponding with a group in the solar spectrum (Fowler and Gregory, *Phil. Trans.*, 1919, [A], 218, 351).

<sup>2</sup> Partington and Shilling, *The Specific Heats of Gases* (Benn, 1924); Shilling, *Trans. Faraday Soc.*, 1926, (vi), 22, 396.

# CONSTANTS OF THE NITROGEN, HYDROGEN, AMMONIA, EQUILIBRIUM.

TABLE A.

*Experimental and Calculated Values of  $10^4 K_p$  at Total Pressure of 1 Atmosphere.*

Temperature, °C.	$10^4 K_p$ , (Haber and le Rossignol.)	$10^4 K_p$ , (Haber and Maschke.)	Calculated by Equation (2).	Calculated by Equation (1).
600	..	13.8	15.2	14.9
700	6.85	6.57	6.84	6.83
750	4.68	..	4.98	4.88
800	3.34	..	3.62	3.59
850	2.86	2.71	2.73	2.71
930	1.89	..	1.84	1.81
1000	1.43	1.39	1.40	1.32
1100	..	0.93	0.93	0.89

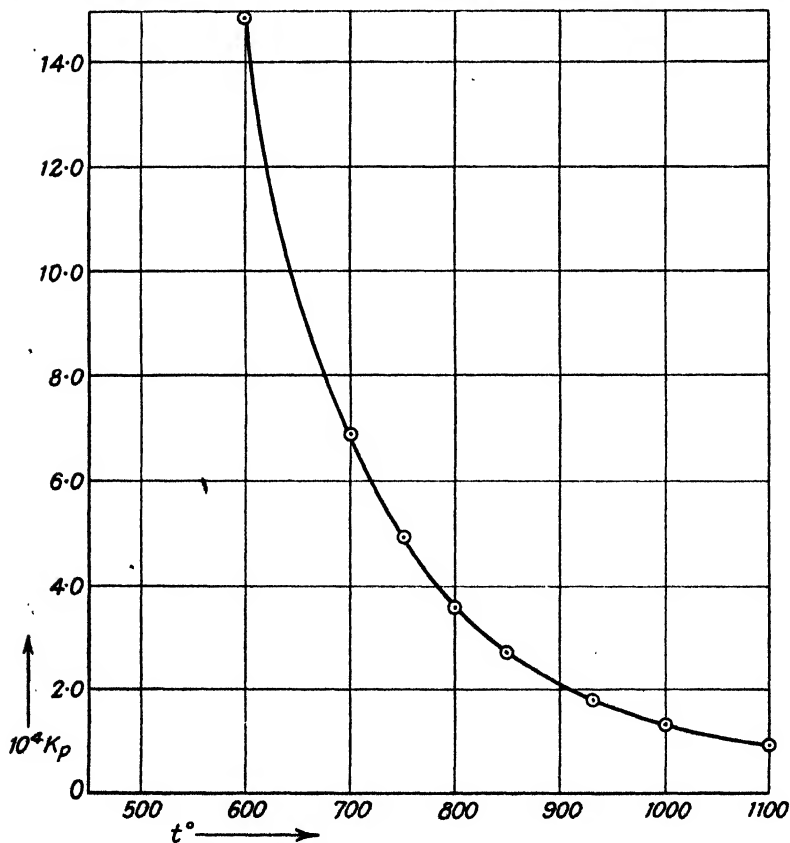


FIG. 12.—Variation in the equilibrium constant of the  $N_2$ ,  $H_2$ ,  $NH_3$ , reaction with temperature. Total pressure = 1 atm.

In Table B the temperatures are those corresponding to the stated values of  $K$ , the total pressure being 1 atmosphere and the composition of the gas  $3\text{H}_2 + \text{N}_2$ .

TABLE B.

*Percentages of Ammonia Formed.*

$10^4 K_p = 200$	100	50	40	30	20	10	9
% $\text{NH}_3 = 0.7$	0.32	0.14	0.11	0.08	0.06	0.032	0.029
$10^4 K_p = 8$	7	6	5	4	3	2	1
% $\text{NH}_3 = 0.025$	0.023	0.019	0.016	0.013	0.0096	0.0065	0.0036

TABLE C.

*Values of  $10^4 K_p$  at a Total Pressure of 30 Atmospheres (Measurements of Haber and le Rossignol, Haber, Tamaru, and Pommaz) (loc. cit., infra).*

$t^\circ \text{C.} = 561$	620	631	700	704	710	722	801	812
$10^4 K_p = 21.3$	12.6	11.4	6.8	6.56	6.46	5.82	3.56	3.38
$t^\circ \text{C.} = 901$	914	952	974					
$10^4 K_p = 2.13$	1.99	1.68	1.48					

The value of the constant should be independent of the total pressures if these are not so high that the participating gases depart widely from the gas laws. Actually there is a fair agreement between Tables C and A. These equilibria were attained in the presence of iron, manganese, nickel, or chromium.

The calculated yields corresponding to various pressures and temperatures are summarised.

TABLE D.

*Calculated Percentage of  $\text{NH}_3$  under various Temperatures and Pressures.*

Temperature, $^\circ \text{C.}$	Percentage of $\text{NH}_3$ .			
	1 Atm.	30 Atm.	100 Atm.	200 Atm.
200	15.3	67.6	80.6	85.8
300	2.18	31.8	52.1	62.8
400	0.44	10.7	25.1	31.3
500	0.129	3.62	10.4	17.6
600	0.049	1.43	4.47	8.25
700	0.0223	0.66	2.14	4.11
800	0.0117	0.35	1.15	2.24
900	0.0069	0.21	0.68	1.34
1000	0.0044	0.13	0.44	0.87

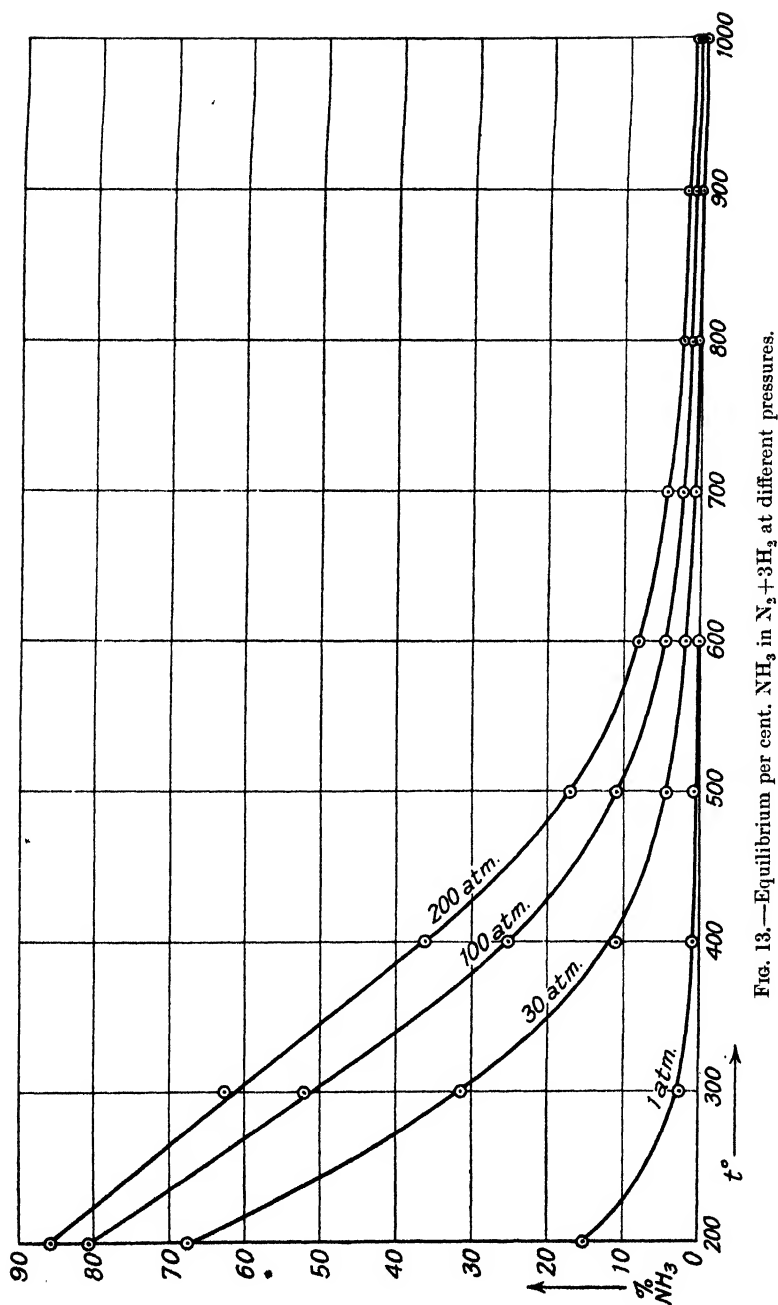


Fig. 13.—Equilibrium per cent.  $\text{NH}_3$  in  $\text{N}_2 + 3\text{H}_2$  at different pressures.

**The Experimental Determinations of the Ammonia Equilibrium.**—Many determinations at atmospheric pressure were carried

out by Haber and co-workers.<sup>1, 2, 3, 4, 5, 6</sup> The mixture of nitrogen and hydrogen was prepared (in one series) by the combustion of air with the theoretical amount of electrolytic hydrogen. This was passed through one of a pair of tubes, each containing a catalyst plug, laid side by side in an electric furnace which maintained a constant temperature over a length of about 6 cm. The proportion of ammonia formed was estimated by absorption in standard acid. In order to approach the equilibrium from the ammonia side, a percentage, say 0.28, which was greater than the equilibrium percentage of ammonia, was added to the mixture, which was passed back through the other tube. When higher pressures were employed the mixture of gases was contained in a cylinder under a pressure of 100 atmospheres. From this, the pressure was reduced to the standard.

Catalyst bombs have been designed for experimental work of this character as well as for continuous production of ammonia. They are constructed of special materials, as, for example, tungsten steel lined with electrolytic iron, since they have to withstand not only very high pressures but also the corrosive action which ammonia has on some commercial irons (see also p. 105).

**Equilibria at High Pressures.**—Since ammonia is formed from its constituent elements with contraction, it follows from the law of mobile equilibrium that an increase in the total pressure should increase the proportion of ammonia formed at each temperature. This result also follows from the assumption of an equilibrium constant. If the expression

$$\frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3 \times p_{\text{N}_2}},$$

or what comes to the same thing, its square root,  $K_p$ , as stated above, is to remain constant when the pressure is increased, then  $p_{\text{NH}_3}$  must increase at the expense of  $p_{\text{H}_2}$  and  $p_{\text{N}_2}$ . This relation is shown by Table D, which is based on the constancy of  $K_p$ . As this increase is advantageous, the values of the constants at high pressures have been investigated experimentally and the relation has been verified.<sup>7, 8</sup>

A mixture of nitrogen and hydrogen was made by burning electrolytic hydrogen and air in the calculated proportions. The gas at 100 atmospheres was purified by a copper deoxidiser with nickel catalyst, and also by passing through soda lime, granular aluminium oxide, and fused potash, and finally through an ammonia catalyst at 500° C. The small amount of ammonia formed carried down with it traces of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . From the observed percentages of ammonia (Table E) it was estimated that the equilibrium constant,

$$K_p = \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{\frac{1}{2}} \times p_{\text{H}_2}^{\frac{3}{2}}},$$

varies with the pressure at a single temperature.<sup>7, 8, 9</sup> This result is

<sup>1</sup> Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1905, **44**, 341.

<sup>2</sup> Haber and le Rossignol, *Ber.*, 1907, **30**, 2144.

<sup>3</sup> Haber and le Rossignol, *Zeitsch. Elektrochem.*, 1913, **19**, 53.

<sup>4</sup> Haber and le Rossignol, *ibid.*, 1915, **21**, 241.

<sup>5</sup> Haber and Maschke, *ibid.*, 1915, **21**, 128.

<sup>6</sup> Haber, Tamaru, and Pommaz, *ibid.*, 1915, **21**, 89.

<sup>7</sup> Larson, *J. Amer. Chem. Soc.*, 1924, **46**, 367.

<sup>8</sup> Larson and Dodge, *ibid.*, 1923, **45**, 2918.

<sup>9</sup> Moldenhauer, *Chem. Zeit.*, 1924, **48**, 233.



not necessarily in disagreement with the law of mass, or concentration, action. For it is known that all gases at high pressures deviate markedly from the gas laws, and it is probable that the active masses calculated from the concentrations present are not identical with the real activities of the gases even at such high temperatures as 500° C.

TABLE E.

*Equilibrium Constants under High Pressures.*

Temperature, ° C.	300 Atm.		600 Atm.		1000 Atm.	
	K.	Per cent. NH <sub>3</sub> .	K.	Per cent. NH <sub>3</sub> .	K.	Per cent. NH <sub>3</sub> .
450	0.00884	35.5	0.01294	53.6	0.02328	69.4
475	0.00674	31.0	0.00895	47.5	0.01493	63.5
500	0.00498	26.2	0.00651	42.1	..	..

Hence it is necessary to split up the general equations which give  $K_p$  as a function of the temperature into series, each characteristic of certain ranges of pressure. Thus :

$$\log K_p = \frac{\alpha}{T} + \beta \log T + \gamma T + \delta T^2 + c.$$

$p$ in Atm.	$\alpha$ .	$\beta$ .	$\gamma \times 10^4$ .	$\delta \times 10^7$ .	$c$ .
300	+2074.8	-2.4943	-1.256	1.8564	2.206
600	"	"	-10.856	"	3.059
1000	"	"	-26.833	"	4.473

From these results the percentages of ammonia formed at 500° C. and at different pressures have been calculated. These are as follows :—

$p$ in atm.	= 10	30	50	100	300	600	1000
NH <sub>3</sub> per cent.	= 1.21	3.49	5.56	10.61	26.44	42.15	57.47

**The Effect of Velocity upon Yield.**—In the investigation of the time factor, a type of apparatus was used which allows the mixture of gases to be circulated at different rates, with continuous refrigeration of the product in order to separate the ammonia formed. This apparatus is similar to that employed in the large scale synthesis of ammonia. Uranium carbide was used as a catalyst,<sup>1, 2</sup> and, in the experiments of Maxted, iron potash.<sup>3</sup> Although of course the maximum yield is that which corresponds to equilibrium, yet it is not desirable in practice to

<sup>1</sup> Haber and le Rossignol, *Zeitsch. Elektrochem.*, 1913, 19, 53.

<sup>2</sup> Haber and Greenwood, *ibid.*, 1915, 21, 241.

<sup>3</sup> Maxted, *J. Soc. Chem. Ind.*, 1918, 37, 232.

allow sufficient time for the equilibrium to be nearly attained, but rather to pass the gases at such a rate that the space-time-yield (S.T.Y.) is a maximum. The S.T.Y. is defined as the yield of ammonia expressed in grams per hour and per c.c. of catalyst space. The space-velocity (S.V.) is the rate of flow in litres per hour at room temperature and atmospheric pressure, per litre of catalyst space. In one series of experiments at  $515^\circ \text{C}$ . and  $p=49.6$  atmospheres pressure, the following results were obtained :—

Time of contact (secs.)=86.0	26.4	10.1	4.3
S.V. $\times 10^3 = 7.6$	24.7	64.8	150.6
$\text{NH}_3$ per cent. = 3.93	3.38	2.77	2.0
S.T.Y. = 0.21	0.6	1.28	2.12

Thus, in spite of the lower percentage of ammonia formed, the space-time-yield is increased by a moderate increase in the velocity of the current of gases.

**The Effect of Velocity.**—An increase of pressure increases both the equilibrium percentage and the reaction velocity. Thus at a pressure of 113.6 atmospheres and a space-velocity of 28.5, the percentage of ammonia is 6.42 and the S.T.Y. is 1.3, which is considerably higher than the comparable second S.T.Y. in the table. In these experiments about 50 per cent. of the total possible percentage of ammonia was formed by a contact of one to two seconds.

**The Catalysts.**—Among the catalysts which induce a sufficient velocity at about  $500^\circ \text{C}$ . (or even below this temperature) are osmium, uranium, uranium carbide, iron, and metals of the iron group, or those similar to iron in their physical properties.

*Osmium* was used in the early experiments of Haber and le Rossignol. It may be in the form of grains, or asbestos may be soaked in an osmium salt, which is then reduced to the finely divided metal. It is too expensive for technical use.

*Uranium.*—The commercial metal may be broken into small pieces, or it may be prepared by the reduction of green uranium oxide with sugar charcoal. These catalysts are easily oxidised by traces of air or water-vapour. Hence they are unsuitable for continuous use. The same may be said of sodamide, which was used in some early experiments, including those in connection with the American plant at Muscle Shoals. Uranium may also be used in the form of the carbide, which is prepared in the electric furnace from the oxide and carbon.

*Cerium.*—The oxide is reduced with magnesium in an atmosphere of hydrogen.

*Tungsten.*—The commercial metal is heated in chlorine, and the chloride is reduced by gaseous ammonia.

*Manganese* in a state of fine division may be prepared from the amalgam. The high initial activity of this catalyst soon falls to a lower constant value.

*Magnesium and Beryllium Cyanamides* may be made by heating the carbonates to  $500^\circ \text{C}$ . in ammonia. They are improved by an admixture of iron.

*Iron.*—This is the catalyst which has been most widely adopted, either alone, or with another metal of the iron group, or with Cr, Mo, W, or with promoters (*vide infra*). Iron may be prepared in a very active form by oxidation in a furnace heated with oxyhydrogen flames. The

oxide is broken up and reduced by hydrogen or ammonia at  $500^{\circ}$  to  $600^{\circ}$  C. It can be freed from catalyst poisons by alternate oxidation and reduction. Iron with molybdenum has been largely used by the Badische Company.

The use of "promoters" with the iron has been found advantageous. These are oxides of the alkaline earth or rare earth metals, alumina, silica, and potassium aluminate. The yield is much improved if two promoters are present, of which one is a basic oxide, such as those of

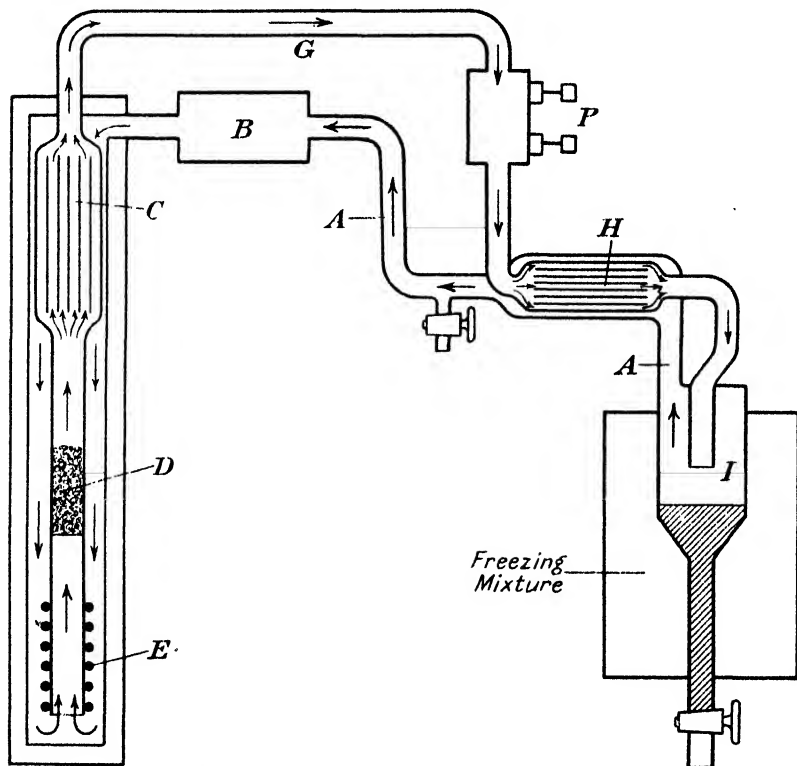


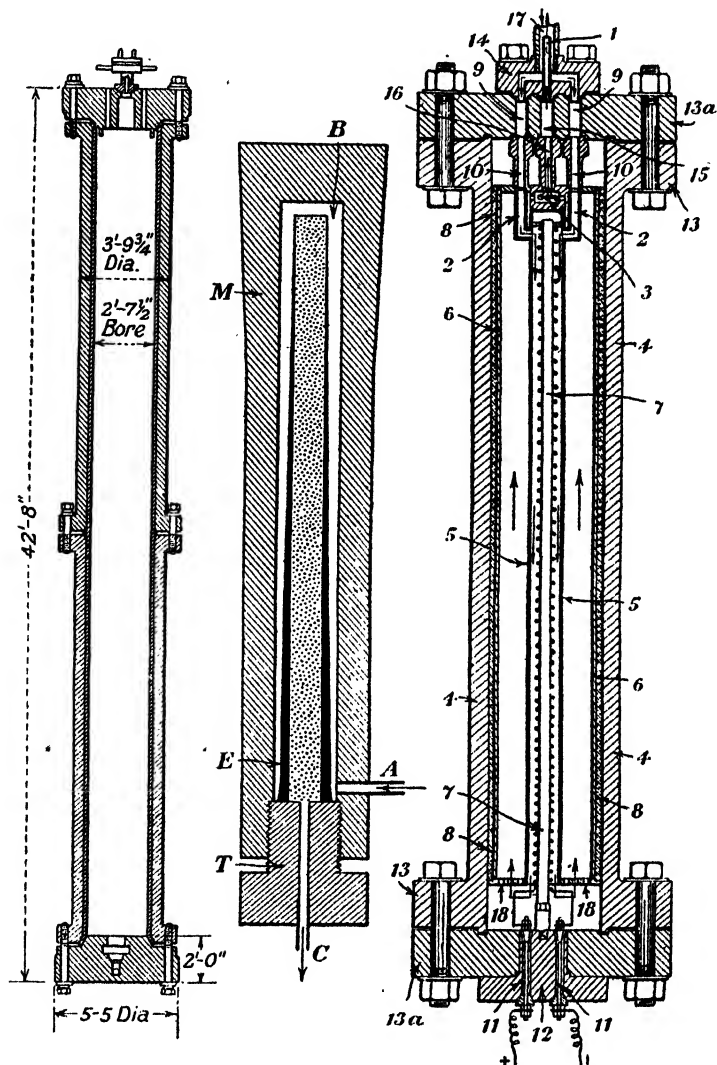
FIG. 14.—Cycle of operations in the synthesis of ammonia (Haber and le Rossignol).

potassium and cesium, and the other a more acidic oxide, such as those of alumina or zirconia. Thus it was found that iron with alumina alone gave a yield of 8 per cent., with potassium oxide alone 5 per cent., but with both together 14 per cent. of ammonia. The manufacture of such a catalyst proceeds in two stages. In the first, iron oxide is fused between water-cooled iron electrodes on a hearth of the oxide. The fused material is mixed with the promoters and reduced in a current of hydrogen.

Some of the modern catalysts are so effective that they allow a sufficient velocity of combination at temperatures slightly above  $300^{\circ}$  C.

**Catalyst Bombs.**—The simplified sketch of the apparatus used by Haber and le Rossignol will give a general idea of the manner in which the combination is effected. The mixture  $N_2 + 3H_2$  enters at A, is dried

by the soda-lime tube B, and passes over the outside of a bundle of steel capillary tubes C. It is thus heated up to  $400^{\circ}$ – $500^{\circ}$  C. by the reacted gases which are flowing inside from the contact mass D, and have a temperature of  $500^{\circ}$  to  $600^{\circ}$  C. The entering gases are further



FIGS. 15-17.

Fig. 15, Haber bomb; fig. 16, Claude bomb; fig. 17, Casale bomb.

heated to  $600^{\circ}$ – $1000^{\circ}$  C. by the electrically heated coil E, then pass through the catalyst D, the capillary tubes C, the connecting tube G, to the pump P, in which they are compressed to 200 atmospheres, and then pass through the inside of the small bore metal tubes H, which are cooled outside by the gas escaping from the liquid ammonia. The

ammonia in the reacted gases then liquefies in the vessel I, the outside of which is kept at  $-60^{\circ}$  to  $-70^{\circ}$  C. by a freezing mixture. The uncombined nitrogen and hydrogen are circulated as before.

The Haber-Bosch bomb as used at Oppau consists of two forgings of tungsten steel held together by bolts (centre of fig. 15). The flanged ends are closed by covers, top and bottom. The over-all dimensions of this bomb are: length 42 ft. 8 in., largest diameter 5 ft. 5 in., and the weight is  $74\frac{1}{2}$  tons. It is lined with electrolytic iron; inside this is refractory material, and inside this another lining. The internal space, of diameter 2 ft.  $7\frac{1}{2}$  in., is occupied by the catalyst. An electrical resistance heater raises the temperature initially to  $600^{\circ}$  C., and then this temperature is largely maintained by the heat of the reaction, conserved by good heat insulation. There is a heat interchanger to reduce the temperature of the issuing gases so that the ammonia at 200 atmospheres can be absorbed in water, giving a 20 per cent. solution. The production is 20 tons of ammonia per day.

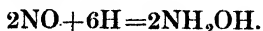
In the Claude bomb (fig. 16) the gases are heated by passing from A round the contact mass, then through this and out at C. The tubes M and T are made of nickel-chromium alloy. Each bomb weighs 15 cwt., and twenty-four of these, weighing 18 tons, are required to make 20 tons of ammonia per day. The reacted gas passes through a coil cooled externally by water, and all the ammonia, except 2 or 3 per cent., is liquefied at the enormous pressure, 900 atmospheres. Fig. 17, the Casale bomb,<sup>1</sup> illustrates some details of heat exchange. The tube 4, with flanged ends 13, is separated from its thin lining 6 by a heat insulator 8. The flanges are closed by plates, of which the lower carries the electrical resistance heater 7 and its electrical connections 11, and the upper the inflow and outflow tubes. The mixture of gases enters the annular space between the thin inner tube 1 and the thick outer tube 17, thus being heated by the reacted mixture which is passing out through 1. The entering gases pass through 9, 10, and 2 to the electrical heater 7, and thence through the perforated plates 18, the catalyst material, the holes 3, and the passages 16 and 15, and out through 1.

<sup>1</sup> Casale and Leprestre, *English Patent*, 176144 (1920).

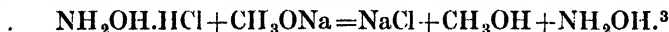
## CHAPTER V.

### HYDROXYLAMINE.

**Historical Methods of Preparation.**—Hydroxylamine hydrochloride was discovered in 1865 by Lossen.<sup>1</sup> This salt was prepared by passing nitric oxide into a solution of hydrochloric acid which was acting on tin with evolution of hydrogen :



Later the salts were prepared in the solid state, and subsequently the free base was isolated by heating the addition compound with zinc chloride,  $\text{ZnCl}_2 \cdot 2\text{NH}_2\text{OH}$ ,<sup>2</sup> or better, by adding sodium methoxide to hydroxylamine hydrochloride in methyl alcohol, and distilling off first the alcohol and then the hydroxylamine at reduced pressure :



The preparations of hydroxylamine generally depend directly or indirectly upon the reduction of more oxidised compounds.

The reduction of nitric oxide can also be effected by hydrogen in platinum sponge over  $100^\circ \text{C}$ .,<sup>4</sup> as well as by nascent hydrogen (*vide supra*).<sup>5, 6</sup> Nitric acid, nitrates, and nitric esters can also be reduced to hydroxylamine by nascent hydrogen formed during the solution of Mg, Zn, etc., in acids, and by the action of water on sodium amalgam,<sup>7, 8, 9, 10</sup> as also by sulphites, sulphides, and cathodic hydrogen (see p. 184). The reduction of nitrites by the same reagents gives a most serviceable method of preparing the salts (*vide infra*). Another method depends upon the reduction of nitro-compounds, such as nitromethane and nitroform.<sup>11, 12, 13</sup>

**The Reduction of Nitrites by Sulphites.**—Crystalline salts formed by the interaction of nitrates and sulphites were prepared and analysed by Fremy.<sup>14</sup> These were later shown to be alkali salts of sulphonie acid derivatives.<sup>15, 16, 17</sup> The direct addition of sulphurous to nitrous acid

<sup>1</sup> Lossen, *Zeitsch. Chem.*, 1865, [2], 1, 551.

<sup>2</sup> Crismer, *Bull. Soc. chim.*, 1890, [3], 3, 115; 1891, 6, 793.

<sup>3</sup> de Bruyn, *Ber.*, 1894, 27, 1867.

<sup>4</sup> Jouve, *Compt. rend.*, 1899, 128, 435.

<sup>5</sup> Ludwig and Hein, *Ber.*, 1869, 2, 671.

<sup>6</sup> Divers and Haga, *Trans. Chem. Soc.*, 1885, 47, 623.

<sup>7</sup> Lossen, *Zeitsch. Chem.*, 1865, [2], 1, 551.

<sup>8</sup> Divers and Haga, *Chem. News*, 1886, 54, 271.

<sup>9</sup> Maumené, *Compt. rend.*, 1870, 70, 147.

<sup>10</sup> Donath, *Ber. Wien. Akad.*, 1877, 75, ii, 566.

<sup>11</sup> Preibisch, *J. prakt. Chem.*, 1874, [1], 8, 309.

<sup>12</sup> Meyer and Locher, *Ber.*, 1875, 8, 219.

<sup>13</sup> Tscherniak, *ibid.*, 1875, 8, 608.

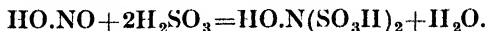
<sup>14</sup> Fremy, *Annalen*, 1845, 56, 315.

<sup>15</sup> Claus, *ibid.*, 1869, 152, 336, 351; 1871, 158, 52, 194.

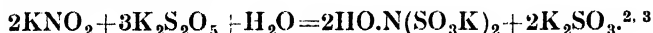
<sup>16</sup> Raschig, *Ber.*, 1887, 20, 584.

<sup>17</sup> Divers and Haga, *Trans. Chem. Soc.*, 1900, 77, 432.

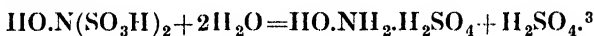
could give dihydroxylamine sulphonic acid,  $(\text{HO})_2\text{N}.\text{SO}_3\text{H}$ , or its anhydride nitroso-sulphonic acid,  $\text{ON}.\text{SO}_3\text{H}$ .<sup>1</sup> Actually, when nitrous acid is added to an acid sulphite, or sulphurous acid is added to a nitrite, hydroxylamine disulphonic acid is produced :



The acid is unstable, but the potassium or sodium salts may be crystallised from the solutions obtained by the interaction of potassium nitrite and metabisulphite at  $0^\circ \text{C}.$  :



The solution, at first neutral, becomes alkaline, and the potassium salt crystallises in rhombic prisms. On acid hydrolysis this gives a salt of hydroxylamine :



A concentrated solution of sodium nitrite (2 mols.) is mixed with one of  $\text{Na}_2\text{CO}_3$  (1 mol.), and sulphur dioxide is passed into the mixture until it is slightly acid. The solution containing  $\text{HO}.\text{N}(\text{SO}_3\text{Na})_2$  is warmed with a little sulphuric acid in order to effect the hydrolysis, which is completed over  $90^\circ \text{C}.$  The resulting solution is neutralised with sodium carbonate, evaporated to small volume, when sodium sulphate (the decahydrate) crystallises. From the mother-liquor a hydroxylamine sulphate crystallises on cooling. Further details about the hydroxylamine-sulphonic acids are given on p. 113.

**Electrolytic Preparation.**—Nitric acid may be reduced to hydroxylamine at a kathode of mercury or amalgamated lead in strongly acid solution, containing say 50 per cent. sulphuric acid and 25 per cent. hydrochloric acid. The nitric acid (50 per cent.) is run slowly into this cooled solution. The yield is over 80 per cent.<sup>4</sup>

**Preparation of the Free Base.**—The base may be prepared in methyl-alcoholic solution as described above. Sodium ethoxide and a solution of ethyl alcohol may also be used, the yield being over 40 per cent.<sup>5</sup> By using an alcohol of higher molecular weight the yield is increased. Thus the fraction distilled from commercial butyl alcohol at  $115.5^\circ$  to  $117.5^\circ \text{C}.$  is converted into sodium butylate. This is added to hydroxylamine hydrochloride in more of the butyl-alcohol fraction, using phenolphthalein as an indicator. The sodium chloride is filtered off and the filtrate cooled to  $0^\circ \text{C}.$ , when hydroxylamine crystallises in large white flakes. It may be purified by distillation under reduced pressure. The base may also be prepared by distillation of the tribasic phosphate,  $(\text{NH}_3\text{O})_3\text{PO}_4$ , in a vacuum. The yield is about 40 per cent.<sup>6</sup>

**Properties of the Base.**—Hydroxylamine is a colourless solid, crystallising in leaves or needles and having a density at  $0^\circ \text{C}.$  of 1.2255 (Bruhl). It melts at  $32^\circ$  to  $33^\circ \text{C}.$  and boils at  $56^\circ$  to  $58^\circ \text{C}.$  under 22 mm.

<sup>1</sup> The crystalline compound, which is precipitated on cooling a hot solution of potassium hydroxylamine sulphate in 22 per cent.  $\text{KNO}_2$  solution, was regarded by Raschig as a derivative of  $(\text{HO})_2\text{N}.\text{SO}_3\text{H}$ , but it is more probably a potassium nitrite hydroxylamine disulphonate,  $\text{KNO}_2.\text{HO}.\text{N}(\text{SO}_3\text{K})_2$  (Divers and Haga, *Trans. Chem. Soc.*, 1900, 77, 432).

<sup>2</sup> Divers and Haga, *ibid.*

<sup>3</sup> Divers and Haga, *ibid.*, 1894, 65, 523.

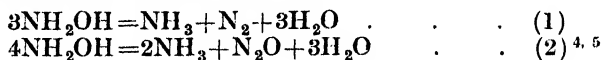
<sup>4</sup> Tafel, *Zeitsch. anorg. Chem.*, 1902, 31, 289.

<sup>5</sup> Lecher and Hofmann, *Ber.*, 1922, 55, 912.

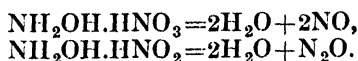
<sup>6</sup> Uhlenhuth, *Annalen*, 1900, 311, 117.

pressure. The density of the vapour under these conditions shows a normal molar weight.<sup>1, 2</sup> The refractive indices for several wave-lengths have been determined; for the sodium line,  $n=1.44047$ . The molecular refraction for the sodium line is 7.228.<sup>2</sup>

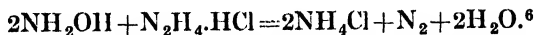
Pure hydroxylamine is deliquescent in air, very soluble in water and in methyl and ethyl alcohols, but scarcely dissolves in typical organic solvents such as ether and chloroform. It may be recrystallised, however, from boiling ether. The solid is very unstable and begins to decompose slowly even at ordinary temperatures, explosively over 100° C.<sup>1, 3</sup> It also decomposes in solution, especially in the presence of alkali. The products are  $\text{NH}_3$ ,  $\text{N}_2$ , and, to a smaller extent,  $\text{N}_2\text{O}$ .



If more combined oxygen is present, as in the nitrate and nitrite, the ammonia is completely oxidised, and the products are nitric and nitrous oxides and water. A comparison of these with the decomposition products of ammonium nitrate and nitrite shows clearly that hydroxylamine is oxyammonia:



**Properties and Reactions of Hydroxylamine Salts.**—*Decomposition of Salts by Heat.*—The hydrochloride decomposes in a somewhat similar manner at about 150° C. In the presence of alkali only a little nitrous oxide is formed, in accordance with equation (1) above. In the presence of acids the reaction is displaced in the direction of equation (2). The change may occur through intermediate compounds: first two molecules of hydroxylamine give hydroxyhydrazine,  $\text{HO.HN.NH}_2$ ; this is converted into the diamide of nitrous acid,  $\text{HIO.N}(\text{NH}_2)$ , which is hydrolysed to ammonia and nitrous acid; the latter reacts with more hydroxylamine to give nitrous oxide. In the presence of hydrazine hydrochloride, hydroxylamine hydrochloride decomposes at about 150° C. The products are nitrogen and ammonium chloride:



*Reactions of Hydroxylamine Salts.*—Hydroxylamine and its salts are powerful reducing agents, the products being oxides of nitrogen, nitrogen, or nitrous acid, according to circumstances. At the same time it is capable of acting as an oxidising agent, especially in alkaline solution, when it is all present as free base. The product of the reaction is then ammonia.

Atmospheric oxygen, especially in the presence of alkali, oxidises it rapidly to oxides of nitrogen. Strong oxidising agents, such as chlorine, potassium permanganate, etc., may cause inflammation. Salts of mercury, silver, gold, and platinum are reduced with precipitation

<sup>1</sup> de Bruyn, *Rec. Trav. chim.*, 1891, 10, 100; 1892, 11, 18.

<sup>2</sup> Bruhl, *Ber.*, 1893, 26, 2508; 1894, 27, 1347.

<sup>3</sup> Tanatar, *Zeitsch. physikal. Chem.*, 1902, 40, 1475.

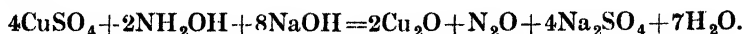
<sup>4</sup> Berthelot, *Compt. rend.*, 1876, 83, 473.

<sup>5</sup> Berthelot and André, *ibid.*, 1890, 110, 830.

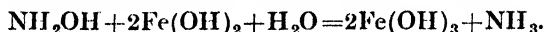
<sup>6</sup> Hofmann and Kroll, *Ber.*, 1924, 57, [B], 937.



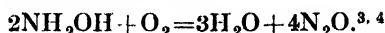
of the metal. Cupric salts are reduced to cuprous oxide in alkaline solution :



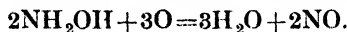
This affords a delicate qualitative test, and also a method of estimating hydroxylamine by means of Fehling's solution.<sup>1</sup> As a qualitative test it is sensitive to 1 in 100,000 parts of solution. Ferrous iron in alkaline solution is oxidised to the ferric state.<sup>2</sup> Thus :



In weakly acid solution ferric chloride is reduced, giving ferrous chloride and nitrous oxide. When boiled with ferric chloride and a moderate amount of acid it is oxidised quantitatively to  $\text{N}_2\text{O}$ . The titration of the ferrous salt with permanganate allows a quantitative determination of the hydroxylamine,



If there is only a small excess of ferric salt the oxidation leads to NO :



In concentrated solutions of sulphuric or phosphoric acids it reacts with ferrous sulphate, giving ferric and ammonium sulphates.<sup>5</sup> It may also be directly oxidised by means of potassium permanganate.<sup>6</sup>

**Thermochemistry.**—The heat of formation of hydroxylamine from its elements is positive and about twice as great as that of ammonia. The value deduced from the heat of combustion of hydroxylamine nitrate is 23,700 cal. per mol.<sup>7</sup> That deduced from the heat of reduction of the hydrochloride by silver nitrate is 24,290 cal.<sup>8</sup>

The heat of neutralisation with strong acids, *e.g.* HCl, in dilute solution is much less—9260 cal.—than that of ammonia—12,300 cal. This is connected with the fact that hydroxylamine is a weaker base than ammonia (*vide infra*). The solution only reacts slightly alkaline.

The heat of formation of the hydrochloride,  $\text{NH}_2\text{OH}.\text{HCl}$ , from its elements is 75,500 cal.<sup>9</sup> or 76,510 cal.,<sup>8</sup> about the same as that of solid ammonium chloride. The greater heat of formation of the free base is almost exactly compensated by the smaller heat of combination with hydrochloric acid.

**Detection and Estimation.**—In addition to the qualitative tests already mentioned, the following have been described. Sodium nitroprusside gives a magenta colour with a neutralised solution.<sup>10</sup> When treated with yellow ammonium sulphide and ammonia it gives an evanescent purple colour. The appearance of this is accelerated by the addition of one or two drops of N/10 manganous sulphate. This test will show 0.00005 per cent. of hydroxylamine.<sup>11</sup> Another test

<sup>1</sup> Jones and Carpenter, *Trans. Chem. Soc.*, 1903, 83, 1394.

<sup>2</sup> Stähler, *Ber.*, 1904, 37, 4732.

<sup>3</sup> Raschig, *Annalen*, 1887, 241, 190.

<sup>4</sup> Bray, Simpson, and Mackenzie, *J. Amer. Chem. Soc.*, 1919, 41, 136.

<sup>5</sup> Hofmann and Kroll, *Ber.*, 1924, 57, [B], 937.

<sup>6</sup> Hofmann and Kuspert, *ibid.*, 1898, 31, 64.

<sup>7</sup> Berthelot and André, *Compt. rend.*, 1890, 110, 830.

<sup>8</sup> Berthelot, *Ann. Chim. Phys.*, 1877, [5], 19, 433.

<sup>9</sup> Thomsen, *Thermochemistry*, transl. by Burke (Longmans, 1908).

<sup>10</sup> Angeli, *Gazzetta*, 1893, 23, ii, 102.

<sup>11</sup> Fischer, *Chem. Zeit.*, 1923, 47, 401.

consists in the addition of an ammoniacal solution of diacetyl monoxime, which is converted into the dioxime by the hydroxylamine, and this is then identified by the formation of a scarlet precipitate with a solution of nickel salt.<sup>1</sup>

In the presence of sodium carbonate or sodium phosphate hydroxylamine is quantitatively oxidised by iodine,<sup>2, 3</sup> and in the absence of other reducing agents it may be determined by means of this reaction. It is also oxidised by iodine in acetic acid solution, but in the presence of hydrochloric acid the reaction is a balanced one; hydroxylamine will liberate iodine from hydrogen iodide.<sup>4</sup>

**Salts of Hydroxylamine.**—Hydroxylamine forms crystallised salts with acids; these are extensively hydrolysed and react acid in aqueous solution. Hydroxylamine is a monacid base, but these salts are only formed in presence of excess of acid. Many characteristic salts, with two or three molecules of the base attached to a monobasic acid, have been prepared. The salts are in most cases moderately soluble in water, very sparingly in ethyl alcohol, insoluble in ether, etc.

The monohydrochloride,  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , is formed in the presence of an excess of hydrochloric acid. It may be crystallised in pointed crystals or leaflets from hot alcohol.<sup>5</sup> The density of the solid is 1.67. The solubility (grams in 100 grams of water) is 45.57 at 17° C.<sup>6</sup> It melts with decomposition at about 150° C. (see p. 109). When a solution of 20 grams of the free base in 260 grams of ethyl alcohol is added to one containing 42 grams of the hydrochloride in 42 c.c. of water, a crystalline precipitate of dihydroxylamine hydrochloride,  $(\text{NH}_2\text{OH})_2 \cdot \text{HCl}$ , is thrown down.

The crystals after washing with alcohol and ether melt at 85° C. They are easily soluble in water. A tribasic salt,  $(\text{NH}_2\text{OH})_3 \cdot \text{HCl}$ , can be prepared by similar methods.<sup>7</sup> Hydroxylamine hydrobromide is made by the double decomposition of the sulphate and barium bromide. It is rather soluble in water. A dihydroxylamine hydrobromide can be made by adding more of the free base.<sup>3</sup> Hydroxylamine hydriodide can be crystallised by evaporation *in vacuo*. It explodes when heated to 83° or 84° C.<sup>8</sup> The dibasic<sup>9</sup> and tribasic<sup>10</sup> hydriodides are more stable.

Hydroxylamine sulphate is obtained by the method of preparation described above, p. 108.<sup>11</sup> It is well crystallised, either in the monoclinic<sup>11</sup> or in the triclinic system.<sup>5</sup> The solubility in water is high; according to Adams,<sup>3</sup> 100 parts of water dissolve the following weights:—

t° C. =	−8	0	10	20	30	40	50	60	90
w =	0.307	0.329	0.366	0.413	0.441	0.482	0.522	0.560	0.685

<sup>1</sup> Hirschel and Verhoeff, *Chem. Weekblad*, 1923, 20, 319.

<sup>2</sup> Haga, *Trans. Chem. Soc.*, 1887, 51, 794, 661.

<sup>3</sup> Adams, *Amer. Chem. J.*, 1902, 28, 198.

<sup>4</sup> Hofmann and Kroll, *Ber.*, 1924, 57, [B], 937.

<sup>5</sup> v. Lang, *Lieb. Annalen Suppl.*, 1868, 6, 226.

<sup>6</sup> Schiff and Monsacchi, *Zeitsch. physikal. Chem.*, 1896, 21, 277.

<sup>7</sup> Lossen, *Annalen*, 1871, 160, 242.

<sup>8</sup> Wolfenstein and Groll, *Ber.*, 1901, 34, 2417.

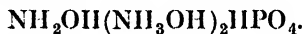
<sup>9</sup> Piloty and Ruff, *ibid.*, 1897, 30, 1656.

<sup>10</sup> Dunstan and Goulding, *Trans. Chem. Soc.*, 1896, 69, 839.

<sup>11</sup> Preibisch, *J. prakt. Chem.*, 1873, [2], 8, 316.

The salt can replace ammonium sulphate in alums, such as aluminium, ferric, and chromic alums. The bisulphate crystallises in prisms from a solution containing the theoretical proportions of the base and acid.<sup>1</sup> The nitrate,  $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ , is prepared in solution by the action of silver nitrate on the hydrochloride or barium nitrate on the sulphate. It is very soluble in water, which only yields the salt in a hygroscopic mass after evaporation and strong cooling. It is decomposed on heating (see p. 108).

The phosphites, phosphates, sub-phosphates, arsenates, vanadates,<sup>2</sup> the dithionate,<sup>3</sup> and the salts of some organic acids,<sup>4,5</sup> are known, as well as the ammonium or potassium hydroxylamine salts of some of these acids. Trihydroxylamine phosphate is more sparingly soluble in water than the salts considered above, the solubility at 20° C. being only 1.9 grams in 100 grams of water. The solution reacts acid. It is noteworthy that the tribasic ammonium phosphate is more difficult to prepare. This fact, taken in conjunction with the easy decomposition of the salt (see p. 108), has led to the belief that it should be formulated as hydroxylamine-dihydroxylamine-hydrogen phosphate,

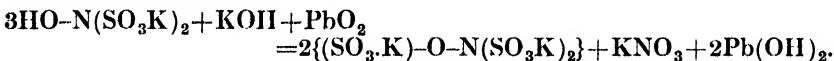


**Addition Compounds.**—Hydroxylamine forms addition compounds, analogous to the amines, with salts of the alkaline earths (including magnesium) and with those of zinc, cadmium, mercury, manganese, cobalt, and nickel.<sup>6</sup> Hydroxylamines of silver and copper, if formed, cannot be isolated on account of the reduction to metals by the hydroxylamine (see this series, Vol. X.). The derivatives of trivalent cobalt, e.g.  $\text{Co}(\text{NH}_2\text{OH})_6\text{Cl}_3$ , are quite analogous to the amines,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  [ $\text{Co}(\text{NH}_3)_5\text{X}]X_2$ , etc.<sup>7,8</sup>

In the platinum series both platinic and platinous derivatives are known. The compound represented by the co-ordinated formula  $[\text{Pt}(\text{NH}_2\text{OH})_4]\text{Cl}_2$  dissociates electrolytically; but  $[\text{Pt}(\text{NH}_2\text{OH})_4](\text{OH})_2$  is not an electrolyte, while the corresponding ammine is one, and reacts alkaline. Also the plato-compound  $[\text{Pt}(\text{NH}_2\text{OH})_2X_2]$  is not an electrolyte.<sup>9,10</sup>

**Sulphonic Derivatives of Hydroxylamine.**—The preparation of hydroxylamine  $\beta\beta$ -disulphonic acid and its salts has already been described (p. 108).

The potassium salt of hydroxylamine  $\alpha\beta\beta$ -trisulphonic acid is made by oxidising that of the  $\beta\beta$ -disulphonic acid with lead peroxide or silver oxide in alkaline solution. Thus :



<sup>1</sup> Divers, *Trans. Chem. Soc.*, 1895, 67, 226.

<sup>2</sup> Hofmann and Kohlschutter, *Annalen*, 1899, 307, 314; also Hofmann, *Zeitsch. anorg. Chem.*, 1898, 16, 463.

<sup>3</sup> Sabanejeff, *ibid.*, 1898, 17, 480.

<sup>4</sup> Lossen, *Lieb. Annalen Suppl.*, 1868, 6, 220.

<sup>5</sup> Simon, *Bull. Soc. chim.*, 1905, [3], 33, 412.

<sup>6</sup> Schlenk and Weichselfelder, *Ber.*, 1915, 48, 669.

<sup>7</sup> Feldt, *ibid.*, 1894, 27, 401.

<sup>8</sup> Berl, *Dissertation*, Zurich, 1901.

<sup>9</sup> Alexander, *Annalen*, 1888, 246, 239.

<sup>10</sup> Uhlenbuth, *ibid.*, 1900, 311, 120.

The reaction probably proceeds through an intermediate violet-coloured nitroso-disulphonate,



A preparation of the potassium salt of the trisulphonic acid has been described in detail.<sup>1</sup> 1200 c.c. of 5N sodium bisulphite is added with stirring to a mixture of 1000 grams of ice and 150 grams of commercial sodium nitrite, the temperature not being allowed to rise above 5° C. The solution is well shaken with 600 grams of lead peroxide and warmed on a water-bath, with continued shaking. The solution is filtered, the filtrate warmed with 800 grams of technical potassium chloride, and the precipitated  $\text{PbCl}_2$  filtered off. The filtrate, after three days, deposits the potassium salt in monoclinic prisms. It is dried on porous plates and over calcium chloride.

The salt crystallises with  $1\frac{1}{2}$  mols. of water and is easily soluble in water. The sodium salt crystallises with 2 mols. of water (monoclinic) and the ammonium salt with  $1\frac{1}{2}$  mols. of water (rhombic). The neutral or alkaline solutions are stable. The acid solutions are hydrolysed on warming, giving as a first product a salt of the  $\alpha\beta$ -disulphonic acid,  $\text{KO}-\text{SO}_2-\text{O}-\text{NH}-\text{SO}_3\text{K}$ . This is isomeric with the  $\beta\beta$ -disulphonate, but differs from it by crystallising anhydrous, and giving no colour with alkaline lead peroxide. It is distinguished from the trisulphonate by its stability at 100° C. The sodium and ammonium salts are also known.<sup>2, 3, 4</sup>

The preparation of the  $\alpha\beta$ -sulphonate is effected by dissolving 423 grams of the dry trisulphonate in 800 c.c. of boiling water which contains 1 c.c. of dilute  $\text{HCl}$ . Any lead sulphate is removed, and the filtrate deposits the potassium salt in colourless crystals, the yield being about 90 per cent. of the theoretical.<sup>1</sup> The salts contain three atoms of alkali metal per molecule of compound or atom of nitrogen, and it is therefore to be supposed that the hydrogen of the imino-group is also replaced, giving, *e.g.*,  $\text{SO}_3\text{K}-\text{O}-\text{NK}-\text{SO}_3\text{K}\cdot 2\text{H}_2\text{O}$ . The partial hydrolysis of this compound may possibly give the mono- $\alpha$ -sulphonic acid,  $(\text{SO}_3\text{H})-\text{O}-\text{NH}_2$ , since the solution at one stage sets free iodine from potassium iodide, a reaction which does not take place with hydroxylamine itself or with the  $\beta$ -acid. The  $\alpha$ -acid might, however, behave as an oxidising agent, since it may be regarded as the amide of permono-sulphuric acid,  $(\text{SO}_3\text{H})-\text{O}-\text{OH}$ .<sup>3</sup> This  $\alpha$ , or isosulphonic acid has been prepared as a microcrystalline powder by the action of chlorsulphonic acid on hydroxylamine hydrochloride.<sup>5</sup>

<sup>1</sup> Raschig, *Ber.*, 1923, 56, [B], 206.

<sup>2</sup> Haga, *Trans. Chem. Soc.*, 1904, 85, 108.

<sup>3</sup> Raschig, *Ber.*, 1906, 39, 245.

<sup>4</sup> Haga, *Trans. Chem. Soc.*, 1906, 89, 240.

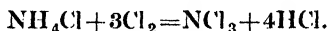
<sup>5</sup> Sommer and Templin, *Ber.*, 1914, 47, 1221.

## CHAPTER VI.

### NITROGEN AND THE HALOGENS.

**Nitrogen Halides.**—The only definite compounds of nitrogen with halogens which have been prepared are the chloride,  $\text{NCl}_3$ , and the iodide,  $\text{N}_2\text{I}_4$ . Nitrogen fluoride was thought to be obtained by the electrolysis of ammonium fluoride,<sup>1</sup> but this was shown later to be the chloride derived from the ammonium chloride as impurity.<sup>2</sup> Nitrogen bromide is stated to be formed by adding potassium bromide to nitrogen chloride under water, when an explosive dark red oil is obtained.<sup>3</sup>

**Nitrogen Chloride,  $\text{NCl}_3$ .**—This compound was first isolated by Dulong in 1811, by the action of chlorine on aqueous ammonium chloride :<sup>4</sup>



The preparation of this explosive substance may be safely effected by inverting a 2-litre flask filled with chlorine over a leaden capsule in a warm saturated solution of ammonium chloride. Small oily drops of the nitrogen chloride form on the sides of the flask and collect in the capsule, while absorption of the ammonium chloride takes place into the flask. Only small quantities of the compound are allowed to accumulate in the capsule, which is removed by tongs and replaced by a fresh one.

Nitrogen trichloride separates at the anode during the electrolysis of a saturated solution of ammonium chloride at  $28^\circ \text{C}$ .<sup>5</sup>

Ammonium chloride reacts with a solution of hypochlorous acid<sup>6</sup> to form nitrogen trichloride, also with sodium hypochlorite,<sup>7</sup> or a suspension of bleaching powder in water (calcium hypochlorite).<sup>8</sup> A convenient method is to add 300 c.c. of a solution (20 per cent.) of ammonium chloride to 3 litres of a suspension of bleaching powder in water containing 22.5 grams of active chlorine saturated with hydrogen chloride. This reaction mixture is shaken with 300 c.c. of benzene, in which the nitrogen trichloride dissolves, and this benzene solution is poured through a filter containing 20 grams of calcium chloride. The dried solution thus obtained contains about 10 per cent. of nitrogen chloride.

A modification of this method is to carry out the experiment at  $0^\circ \text{C}$ ., omitting the hydrogen chloride and the benzene.<sup>9</sup>

<sup>1</sup> Warren, *Chem. News*, 1887, 55, 289.

<sup>2</sup> Ruff and Geisel, *Ber.*, 1903, 36, 2677.

<sup>3</sup> Millon, *Ann. Chim. Phys.*, 1838, [2], 69, 75.

<sup>4</sup> Dulong, *Ann. Chim.*, 1813, 86, 37. See also Noyes and Lym, *Amer. Chem. J.*, 1900, 23, 460; Bray and Dowell, *J. Amer. Chem. Soc.*, 1917, 39, 905.

<sup>5</sup> Kolbe, *J. prakt. Chem.*, 1847, 41, 137; Meyer, *Ber.*, 1886, 21, 26; Hofer, *Chem. Zeit.*, 1896, 20, 470.

<sup>6</sup> Balard, *Ann. Chim. Phys.*, 1834, (ii), 57, 225.

<sup>7</sup> Hentschel, *Ber.*, 1897, 30, 1434, 1792.

<sup>8</sup> Hentschel, *ibid.*, 1897, 30, 2642.

<sup>9</sup> Rai, *Chem. News*, 1918, 253.

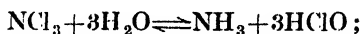
Anhydrous ammonia and chlorine react to give nitrogen trichloride, much of which decomposes into nitrogen and chlorine either directly or by the action of the ammonia.<sup>1</sup>

*Properties.*—Nitrogen chloride is a yellow volatile oil with a pungent smell resembling chlorine, the vapour of which attacks the eyes and mucous membrane. The density is 1.653 and boiling-point 71° C. When heated above 93° C. it decomposes explosively into its elements. It explodes violently when exposed to strong light or when brought into contact with many substances, such as ozone, phosphorus, arsenic, alkalies, and organic matter. Thus a feather dipped in turpentine and applied to a small drop of the oil detonates it immediately. Generally speaking, it is stable in the presence of metals, strong acids, resins, and sugars. Organic solvents dissolve nitrogen chloride, giving highly refracting yellow solutions which are stable in the dark, but gradually decompose when exposed to light.

Many experimenters have suffered from the explosive properties of this substance, including Dulong, Faraday, and Davy.

The heat of formation is given as  $-38.477$  Cals.<sup>2</sup> A more recent determination gives the heat of formation of the compound in carbon tetrachloride from gaseous nitrogen and gaseous chlorine as  $-54.700$  Cals.<sup>3</sup>

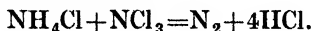
Nitrogen chloride is hydrolysed by water to ammonia and hypochlorous acid,<sup>4</sup>



which is probably an explanation of the ready formation of ammonia, and also of the greater solubility of the compound in hydrochloric acid than in sulphuric acid, as the former reacts with the hypochlorous acid. Thus, when a carbon-tetrachloride solution of nitrogen chloride is shaken with moderately concentrated hydrochloric acid and the aqueous solution (freed from excess  $\text{NCl}_3$ ) boiled with potassium hydroxide, a quantity of ammonia is evolved:<sup>5</sup>



The benzene solution of nitrogen chloride may be used as a chlorinating agent for organic compounds.<sup>6</sup> Aqueous solutions of ammonium chloride decompose nitrogen chloride—the concentrated solution quickly and the dilute solution more slowly:



*Constitution.*—The formula  $\text{NCl}_3$  was first assigned by Dulong,<sup>7</sup> although Davy<sup>8</sup> considered that there was chlorine in excess of that required by this formula, while some later investigators concluded that

<sup>1</sup> Noyes and Haw, *J. Amer. Chem. Soc.*, 1920, 42, 2167.

<sup>2</sup> Troost, *Compt. rend.*, 1868, 69, 204.

<sup>3</sup> Noyes, *J. Amer. Chem. Soc.*, 1925, 47, 1336.

<sup>4</sup> Seliwanow, *Ber.*, 1894, 27, 1012.

<sup>5</sup> Chapman and Vodden, *Trans. Chem. Soc.*, 1909, 95, 41.

<sup>6</sup> Hentschel, *Ber.*, 1897, 30; 1898, 31, 240.

<sup>7</sup> Dulong, *Schweigger's J.*, 1812, 8, 32.

<sup>8</sup> Davy, *Phil. Trans.*, 1813, 103, 1, 242.

hydrogen was also present.<sup>1</sup> Gattermann,<sup>2</sup> however, found that the amount of chlorine present closely agreed with that for  $\text{NCl}_3$ , by decomposing nitrogen trichloride with ammonia, and estimating the chlorine in the resulting ammonium chloride as silver chloride. This result has been confirmed.<sup>3</sup>

**Nitrogen Iodide,  $\text{N}_2\text{H}_3\text{I}_3$ .**—A very explosive compound of nitrogen and iodine, discovered by Courtois in 1812, was investigated later by Serullas,<sup>4</sup> who prepared it by the action of an alcoholic solution of iodine on aqueous ammonia.

The action of strong ammonia solution on solid iodine also produces the substance as a black powder, which can be filtered off.<sup>5</sup>

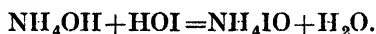
Alcoholic solutions of iodine and ammonia produce the same compound.<sup>6</sup>

A convenient method is to add gradually a solution of iodine in potassium iodide to aqueous ammonia, when a black precipitate separates.<sup>7</sup>

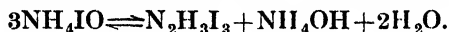
The reaction between iodine and ammonia appears to proceed in three stages.<sup>8</sup> Firstly, hypoiodous acid and ammonium iodide are produced :



and the hypoiodous acid further combines with ammonia to form ammonium hypoiodite :



Finally, the ammonium hypoiodite decomposes into nitrogen iodide :



The last reaction is apparently reversible, as the nitrogen iodide redissolves in strong ammonia.<sup>9</sup>

Ammonium iodide and bleaching-powder solutions also give the explosive nitrogen iodide.<sup>10</sup>

**Properties.**—Nitrogen iodide exists in the form of flattened needles which are copper-coloured by reflected light and red by transmitted light, with a density of 3.5. It is one of the most explosive of substances; when dry it will explode spontaneously or by the lightest contact, even that of a feather. Warming or exposure to strong light also causes its explosive decomposition, and in all its reactions it tends to break down into nitrogen and hydrogen iodide.

The composition of nitrogen iodide has been the subject of much investigation, but it seems that the usual product of ammonia and iodine is  $\text{NI}_3 \cdot \text{NH}_3$ . Sodium sulphite is oxidised to the sulphate according to the following equation :—

<sup>1</sup> Porret, Wilson, and Kirk, *Gilbert's Annalen*, 1813, 47, 56, 69; Gladstone, *Trans. Chem. Soc.*, 1854, 7, 51.

<sup>2</sup> Gattermann, *Ber.*, 1888, 21, 755.

<sup>3</sup> Chapman and Vodden, *Trans. Chem. Soc.*, 1909, 95, 138.

<sup>4</sup> Serullas, *Ann. Chim. Phys.*, 1829, (ii), 42, 200.

<sup>5</sup> Stas, *Gesetze der Proportionen*, Leipzig, 1867, p. 138.

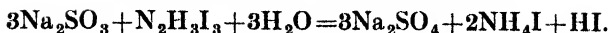
<sup>6</sup> Bunsen, *Annalen*, 1852, 84, 1.

<sup>7</sup> Schönbein, *J. prakt. Chem.*, 1861, 84, 385; Guyard, *Compt. rend.*, 1883, 97, 526; *Ann. Chim. Phys.*, 1884, [6], 1, 358.

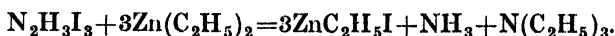
<sup>8</sup> Seliwanow, *Ber.*, 1894, 27, 1012.

<sup>9</sup> Chattaway and Orton, *Amer. Chem. J.*, 1900, 24, 331.

<sup>10</sup> Gladstone, *loc. cit.*

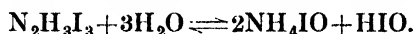


The reaction between nitrogen iodide and zinc ethyl confirms the composition  $\text{N}_2\text{H}_3\text{I}_3$ :<sup>1</sup>



A black explosive compound is obtained when silver nitrate is added to nitrogen iodide suspended in water,<sup>2</sup> which has the composition  $\text{NI}_3 \cdot \text{AgNH}_2$ .<sup>1</sup>

The hydrolysis of nitrogen iodide by water proceeds according to the equation<sup>3</sup>



Many substances are readily oxidised by nitrogen iodide: hydrogen iodide liberates iodine, hydrogen chloride forms iodine chloride, hydrogen cyanide gives iodine cyanide,  $\text{ICN}$ , and alkalis form a mixture of iodide and iodate.

At low temperatures a number of addition compounds of nitrogen iodide can be produced, such as  $\text{NI}_3 \cdot 2\text{NH}_3$ ,  $\text{NI}_3 \cdot 3\text{NH}_3$ , and  $\text{NI}_3 \cdot 12\text{NH}_3$ .<sup>3</sup>

**Monochloramine,  $\text{NH}_2\text{Cl}$ .**---Gattermann<sup>4</sup> came to the conclusion that the chlorination of ammonia occurs in three stages:

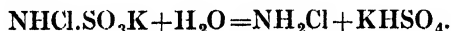
- (1)  $\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl} (\text{monochloramine}) + \text{HCl},$
- (2)  $\text{NH}_2\text{Cl} + \text{Cl}_2 = \text{NHCl}_2 (\text{dichloramine}) + \text{HCl},$
- (3)  $\text{NHCl}_2 + \text{Cl}_2 = \text{NCl}_3 (\text{trichloramine}) + \text{HCl};$

but it was not found possible to isolate either mono- or di-chloramine by this method. Raschig,<sup>5</sup> however, prepared monochloramine by mixing dilute equimolecular solutions of ammonia and sodium hypochlorite, and distilling the mixture at low temperatures in a vacuum:



An unstable yellow liquid is obtained which can be solidified into colourless unstable crystals with melting-point  $-66^\circ \text{C}$ .

Monochloramine is also produced by the hydrolysis of potassium chloramino-sulphonate with dilute mineral acids:



Monochloramine is decomposed by alkalis with the formation of ammonia and nitrogen:

- $$\begin{cases} \text{(i)} & 3\text{NH}_2\text{Cl} + 3\text{KOH} = \text{NH}_3 + \text{N}_2 + 3\text{KCl} + 3\text{H}_2\text{O}, \\ \text{(ii)} & 3\text{NH}_2\text{Cl} + 2\text{NH}_3 = \text{N}_2 + 3\text{NH}_4\text{Cl}; \end{cases}$$

but at the same time some of the ammonia reacts with the chloramine to produce a small amount of hydrazine hydrochloride:



Monochloramine reacts with potassium iodide to form nitrogen iodide.

<sup>1</sup> Silberrad, *Trans. Chem. Soc.*, 1905, 87, 55, 66.

<sup>2</sup> Szuhay, *Ber.*, 1893, 26, 1933.

<sup>3</sup> Hugot, *Ann. Chim. Phys.*, 1900, (vii), 21, 5; Ruff, *Ber.*, 1900, 33, 3025.

<sup>4</sup> Gattermann, *ibid.*, 1888, 21, 755.

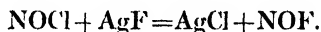
<sup>5</sup> Raschig, *Verh. Ges. deut. Naturforsch. Aerzte*, 1907, 11, i, 120.



## CHAPTER VII.

### OXY-HALOGEN DERIVATIVES OF NITROGEN.

**Nitrosyl Fluoride, NOF.**—Nitrosyl fluoride is prepared by passing nitrosyl chloride over silver fluoride in a platinum tube heated to  $200^{\circ}$ – $250^{\circ}$  C., and condensing the gas in a platinum receiver immersed in liquid air. The liquid is purified by fractional distillation at a low temperature : <sup>1</sup>

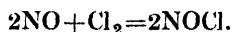


*Properties.*—At ordinary temperatures nitrosyl fluoride is a colourless gas, which liquefies at  $-56^{\circ}$  C. and solidifies at  $-134^{\circ}$  C. The vapour density (compared with air as unity) at 760 mm. and  $23^{\circ}$  C. is 1.683, which agrees with the formula NOF.

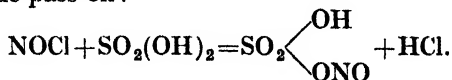
Chemically the gas is very active, many substances reacting with it in the cold. Thus sodium, silicon, boron, phosphorus, and antimony inflame, producing the corresponding fluoride and evolving nitric oxide. Lead, antimony, bismuth, and copper are only slowly attacked; while sulphur, carbon, and iodine are without action even on heating. Arsenic and antimony pentafluorides form additive compounds with nitrosyl fluoride. <sup>2</sup>

The gas fumes in moist air, owing to the formation of hydrogen fluoride and nitrous acid, which decomposes, producing brown fumes.

**Nitrosyl Chloride, NOCl.**—(1) Nitrosyl chloride may be prepared in many ways. It was first prepared by Gay-Lussac by the direct union of nitric oxide and chlorine : <sup>3</sup>



(2) The most convenient method for producing pure nitrosyl chloride is by the decomposition of aqua-regia. <sup>4</sup> A mixture of 1 volume of concentrated nitric acid (sp. gr. 1.42) and 4 volumes of hydrochloric acid (sp. gr. 1.16) is gently warmed, and the nitrosyl chloride and chlorine dried by means of calcium chloride. The dried mixture of gases is then led into concentrated sulphuric acid, which forms nitrosyl-sulphuric acid with the nitrosyl chloride, while the chlorine and some hydrogen chloride pass on :



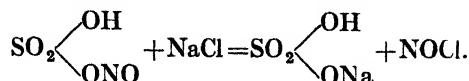
<sup>1</sup> Ruff and Stäuber, *Zeitsch. anorg. Chem.*, 1905, 47, 190.

<sup>2</sup> Ruff and Stäuber, *ibid.*; 1908, 58, 325.

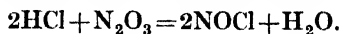
<sup>3</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1848, [3], 23, 203. See also Wourtzet, *J. Chim. phys.*, 1913, 11, 214; Trautz, *Zeitsch. anorg. Chem.*, 1914, 88, 285; Francesconi and Bresciani, *Atti R. Accad. Lincei*, 1903, [5], 12, II, 75; Boubaoiff and Guye, *J. Chim. phys.*, 1911, 9, 290.

<sup>4</sup> Tilden, *Trans. Chem. Soc.*, 1860, 13, 630; Girard and Pabst, *Bull. Soc. chim.*, 1878, (ii), 30, 531.

The nitrosyl-sulphuric acid is decomposed by dropping the saturated sulphuric-acid solution on to dry sodium chloride :



(3) Dry hydrogen chloride passed into liquid nitrogen trioxide evolves nitrosyl chloride, which is not quite pure :<sup>1</sup>

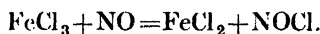


The following methods have been used for the preparation of nitrosyl chloride, but none of them give as pure a product as that given under (2) :—

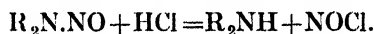
(4) Distillation of potassium nitrite with phosphorus pentachloride :



(5) Nitric oxide decomposes ferric chloride at a high temperature :<sup>2</sup>



(6) Nitrosamines react with hydrogen chloride :<sup>3</sup>



*Properties.*—Nitrosyl chloride is a yellow gas at ordinary temperatures, with a suffocating odour. It is readily liquefied by passing through a tube immersed in a freezing mixture, and a red liquid is obtained which boils at  $-5.5^\circ \text{C}$ . at 760 mm.<sup>1</sup> The chloride is obtained as a yellow solid by further cooling. The melting-point is variously given as  $-65^\circ$ ,<sup>4</sup>  $-60^\circ$  to  $-61^\circ \text{C}$ .<sup>5</sup>

The variation in density of liquid nitrosyl chloride with temperature is given in the following table :—<sup>6</sup>

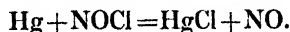
Temperature, $^\circ \text{C}$ .	$-12$	$-15$	$-18$	$-55$
Density . . .	1.4165	1.4250	1.4330	1.550

The critical temperature is  $163^\circ$  to  $164^\circ \text{C}$ .<sup>5</sup>

Nitrosyl chloride does not begin to dissociate until the relatively high temperature of  $700^\circ \text{C}$ . is reached.<sup>7</sup> The dissociation into nitric oxide and chlorine is attended with the absorption of  $-14.4$  Cals.<sup>1</sup>

The absorption spectrum shows three bands in the red and three feeble bands in the extreme green.<sup>8</sup>

Nitrosyl chloride is immediately decomposed by water with the formation of hydrochloric and nitric acids. Most metals react with the gas (gold and platinum are unaffected) to give the metallic chloride and nitric oxide :



<sup>1</sup> Briner and Pytkov, *J. Chim. phys.*, 1912, **10**, 640.

<sup>2</sup> Thomas, *Compt. rend.*, 1895, **120**, 447.

<sup>3</sup> Lachmann, *Ber.*, 1900, **33**, 1035.

<sup>4</sup> van Heteren, *Zeitsch. anorg. Chem.*, 1900, **22**, 277.

<sup>5</sup> Francesconi and Bresciani, *Atti R. Accad. Lincei*, 1903, [5], **12**, II, 75.

<sup>6</sup> Geuther, *Annalen*, 1888, **245**, 96; Briner and Pytkov, *loc. cit.*

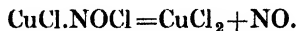
<sup>7</sup> Sudborough and Miller, *Chem. News*, 1890, **62**, 307.

<sup>8</sup> Magnanini, *Zeitsch. physikal. Chem.*, 1889, **4**, 427.

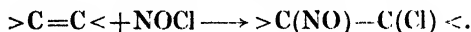
Metallic oxides and hydroxides form corresponding nitrites and chlorides :<sup>1</sup>



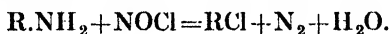
Many metallic chlorides form additive compounds with nitrosyl chloride, *e.g.*  $\text{CuCl}.\text{NOCl}$ ,  $\text{BiCl}_3.\text{NOCl}$ ,  $\text{ZnCl}_2.\text{NOCl}$ ,  $\text{FeCl}_3.\text{NOCl}$ ,  $\text{SnCl}_4.2\text{NOCl}$ ,  $\text{SbCl}_3.5\text{NOCl}$ ,  $\text{AuCl}_3.\text{NOCl}$ ,  $\text{PtCl}_4.\text{NOCl}$ . The last two compounds are stable towards heat and may be sublimed, but the majority of these substances decompose on heating with evolution of chlorine or nitric oxide :



Unsaturated organic compounds also form additive compounds :



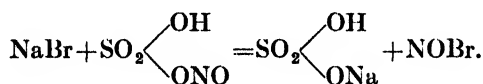
Amines are decomposed with the formation of chlorides and evolution of nitrogen :<sup>2</sup>



Sulphur trioxide reacts with nitrosyl chloride to form nitroso-sulphuryl chloride.

**Nitrosyl Bromide, NOBr.**—The direct union of nitric oxide with bromine occurs when the gas is led into bromine till no further absorption takes place at temperatures between  $-7^\circ$  and  $-15^\circ \text{C}$ .<sup>3</sup> If the temperature is above  $-7^\circ \text{C}$ ., the additive compound  $\text{NOBr}.\text{Br}_2$  is formed.

Sodium bromide and nitrosyl sulphuric acid react to form nitrosyl bromide :<sup>4</sup>



**Properties.**—Nitrosyl bromide is a brownish-black liquid, boiling at  $-2^\circ \text{C}$ . with dissociation. Generally speaking, nitrosyl bromide shows very similar properties to nitrosyl chloride.

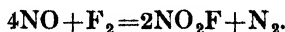
The heat of formation of nitrosyl bromide is between 9·000 and 10·500 Cals.<sup>5</sup>

The fusion curve of bromine and nitric oxide shows a eutectic at  $-40^\circ \text{C}$ . corresponding to  $\text{NOBr}_3$  or  $\text{NOBr}.\text{Br}_2$ , and another at  $-55^\circ \text{C}$ . which corresponds to  $\text{NOBr}_2$  and  $\text{NOBr}$ .

The compound  $\text{NOBr}_3$  is a brownish opaque liquid which boils at  $32^\circ \text{C}$ . with decomposition. The density at  $20^\circ \text{C}$ . is 2·637.

The heat of formation at  $22^\circ \text{C}$ . is 27·000 Cals.<sup>5</sup>

**Nitryl Fluoride,  $\text{NO}_2\text{F}$ .**—This compound is obtained by the action of nitric oxide on fluorine at the temperature of liquid air :<sup>6</sup>



<sup>1</sup> Sudborough, *Trans. Chem. Soc.*, 1891, 59, 655.

<sup>2</sup> Solonina, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 431.

<sup>3</sup> Landolt, *Annalen*, 1861, 116, 177.

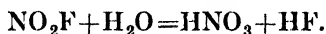
<sup>4</sup> Girard and Pabst, *Bull. Soc. chim.*, 1878, (ii), 30, 531.

<sup>5</sup> Trautz and Dalal, *Zeitsch. anorg. Chem.*, 1920, 110, 1.

<sup>6</sup> Moissan and Lebeau, *Compt. rend.*, 1905, 140, 1573, 1621.

At ordinary temperatures nitryl fluoride is a colourless, pungent-smelling gas, which attacks the mucous membrane. The liquid boils at  $-63.5^{\circ}\text{C}.$ , and solidifies at  $-139^{\circ}\text{C}.$  to a colourless solid. The vapour density is 2.24 (compared with air=1), which is almost identical with that required by the formula  $\text{NO}_2\text{F}$  (2.26).

The gas is very reactive, and attacks many metals and non-metals, such as arsenic, antimony, aluminium, iron, mercury, alkali and alkaline earth metals, phosphorus, boron, and silicon. It has no action on hydrogen, sulphur, or carbon. Water decomposes nitryl fluoride with the quantitative formation of nitric and hydrofluoric acids:



Many organic compounds react with nitryl fluoride.

**Nitryl Chloride,  $\text{NO}_2\text{Cl}$ ,** was stated to have been obtained by the action of nitrogen tetroxide on chlorine<sup>1</sup> or hydrogen chloride,<sup>2</sup> and by the action of chlorine on silver nitrate.<sup>3</sup> Similarly, nitryl bromide,  $\text{NO}_2\text{Br}$ , was considered to be the product of the action of bromine on nitrogen tetroxide.<sup>1</sup> Later investigations, however, appeared to disprove the formation of these halogen compounds by the above methods.<sup>4</sup> More recently, it is claimed that nitryl chloride is formed when nitric acid reacts with phosphorus oxychloride, and nitryl bromide by passing nitrogen tetroxide and bromine vapour over a catalyst of calcined lime heated to  $200^{\circ}$ – $250^{\circ}\text{C}.$ <sup>5</sup>

<sup>1</sup> Hasenbach, *J. prakt. Chem.*, 1871. (ii), 4, 1.

<sup>2</sup> Muller, *Annalen*, 1862, 122, 1.

<sup>3</sup> Odet and Vignon, *Compt. rend.*, 1870, 70, 96.

<sup>4</sup> Gutbier and Lehmann, *J. prakt. Chem.*, 1905, (ii), 71, 180.

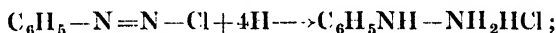
<sup>5</sup> Zuskine, *Bull. Soc. chim.*, 1925, (iv), 37, 187.

## CHAPTER VIII.

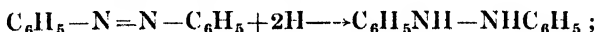
### HYDRIDES AND THEIR DERIVATIVES CONTAINING TWO OR MORE NITROGEN ATOMS.

#### HYDRAZINE.

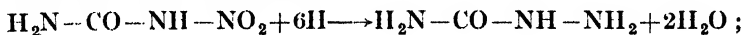
**History.**— Organic derivatives of hydrazine have long been known and used in syntheses, as, for example, that of phenylhydrazones from hydrazine. The substituted hydrazines are obtained by the reduction of compounds containing the diazo grouping; thus, diazo-benzene chloride may be reduced to phenylhydrazine hydrochloride,



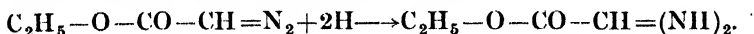
azo-benzene yields diphenylhydrazine,



nitro-urea yields semi-carbazide,

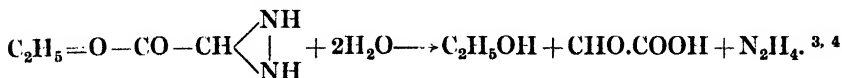


diazo-acetic ester yields hydrazo-acetic ester,

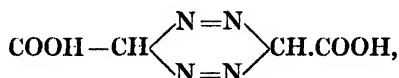


Hydrazine itself was prepared by Curtius in 1887<sup>1</sup> from di-diazo-acetic acid. Para-urazinc,  $\text{C}_2\text{H}_4\text{O}_2\text{N}_4$ , derived from urea, may also be hydrolysed by dilute sulphuric acid and the sulphate of hydrazine crystallised out.<sup>2</sup> When ethyl-diazo-acetate is heated with concentrated potash a coloured salt is formed. After digestion with sulphuric acid the colour disappears and hydrazine sulphate is formed.

**Preparation.**— (1) By the reduction and subsequent hydrolysis of diazo-acetic ester, or by the hydrolysis of its condensation products. Diazo-acetic ester is reduced by an alkaline ferrous solution to hydrazo-acetic ester (*vide supra*), which is then hydrolysed by mineral acids:



Diazo-acetic ester and the free acid easily polymerise into bisdiazo-compounds:



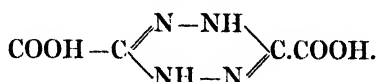
<sup>1</sup> Curtius, *Ber.*, 1887, 20, 1632.

<sup>2</sup> Chattaway, *Trans. Chem. Soc.*, 1909, 95, 237.

<sup>3</sup> Curtius and Jay, *J. prakt. Chem.*, 1889, [2], 39, 27, 107.

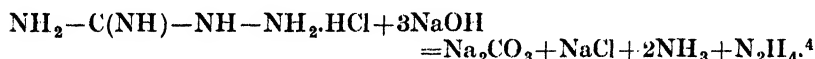
<sup>4</sup> v. Pechmann, *Ber.*, 1895, 28, 1847.

which probably undergo a tautomeric change, giving

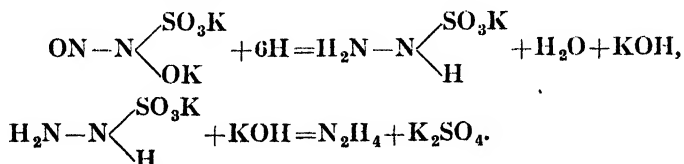


This compound, on boiling with mineral acids, is hydrolysed (by 4 mols. of water) to  $2(\text{COOH})_2 + 2\text{N}_2\text{H}_4$ .<sup>1,2</sup> 245 grams of the bisdiaz acid in 2 litres of water and 300 grams of concentrated sulphuric acid are heated on the water-bath until all is dissolved, then heated until effervescence ( $\text{CO}_2$ ) ceases. On cooling, hydrazine sulphate crystallises.<sup>3</sup>

(2) By the reduction of nitro-guanidine to amino-guanidine, which is then hydrolysed. Ammonium thiocyanate is heated for some time at  $170^\circ$  to  $180^\circ$  C. The residue, guanidine-thiocyanate,  $\text{NH}_2-\text{C}(\text{NH})-\text{NH}_2.\text{HNCS}$ , is treated, first with concentrated, then with fuming, sulphuric acid. This mixture, after cooling, is mixed with nitric acid of density 1.5 and poured into water. Nitro-guanidine,  $\text{NH}_2-\text{C}(\text{NH})-\text{NH}-\text{NO}_2$ , separates, and is reduced with zinc dust and acetic acid. The solution of amino-guanidine,  $\text{NH}_2-\text{C}(\text{NH})-\text{NH}-\text{NH}_2$ , may be hydrolysed either by acids or by alkalis. It is concentrated, mixed with sodium-hydroxide solution, and boiled for eight to ten hours. The cooled liquid, after separation from  $\text{NaHCO}_3$ , is mixed with concentrated sulphuric acid, when most of the hydrazine separates as the sulphate, and may be purified by one recrystallisation :



(3) By the reduction of hyponitrous<sup>5</sup> acid or its sulphonie derivative.<sup>6,7</sup> The hyponitrous acid may be reduced by zinc and acetic acid in the presence of sodium bicarbonate.<sup>5</sup> Or, the potassium salt of nitroso-sulphurous acid (nitroso-hydroxylamine sulphonie acid),  $2\text{NO.K}_2\text{SO}_3$  (or  $\text{KO}-\text{N}=\text{NO}-\text{SO}_3\text{K}$ ), which was discovered by Davy, may be prepared by passing nitric oxide to saturation into an alkaline solution of potassium sulphite containing an excess of potassium hydroxide. The compound is deposited in a crystalline form, and may be recrystallised from hot water with some loss. A solution of this salt may be reduced with an excess of sodium amalgam :<sup>6,7</sup>



Several organic compounds containing the  $-\text{N}=\text{N}-$  group and the  $-\text{SO}_3\text{K}$  group are hydrolysed in this way by alkalis.

<sup>1</sup> Hantzsch and Silberrad, *Ber.*, 1900, 33, 58.

<sup>2</sup> Hantzsch and Lehmann, *ibid.*, 1901, 34, 2506; 1900, 33, 3688.

<sup>3</sup> Curtius and Jay, *loc. cit.*

<sup>4</sup> Thiele, *Annalen*, 1892, 270, 1.

<sup>5</sup> Brackel, *Ber.*, 1900, 33, 2115.

<sup>6</sup> Duden, *ibid.*, 1894, 27, 3498.

<sup>7</sup> Divers and Haga, *Trans. Chem. Soc.*, 1896, 69, 1610.

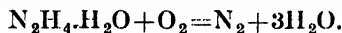
(4) By the oxidation of ammonia with sodium hypochlorite in the presence of glue.<sup>1</sup> One litre of an aqueous solution of sodium hypochlorite is mixed with 3 litres of concentrated ammonia solution containing 12 c.c. of a 5 per cent. solution of glue. The mixture is boiled in an open vessel for about half an hour, cooled in ice, and acidified with 10 per cent. sulphuric acid. The sulphate,  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ , crystallises. The yield (80 to 90 grams) is about 40 per cent. of theory. The oxidation of the ammonia probably proceeds through the formation of chloramine,



The glue appears to act as a protective colloid, and also by raising the viscosity of the solution.<sup>2, 3</sup>

**The Hydrate and the Free Base.**—Hydrazine is set free by alkalies in aqueous solution in the hydrated form. One molecule of water is firmly combined, for on distillation of the salts with solid potassium hydroxide, the hydrate,  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , is obtained as a fuming liquid which boils at  $188^\circ \text{C}$ .<sup>4, 5</sup> This is sometimes regarded as a constant boiling mixture, *i.e.* one of maximum boiling-point, like those of the halogen hydracids and water. It has been proved that there is dissociation in the vapour phase. The hydrate does not freeze at  $-40^\circ \text{C}$ .; it does not exist as a definite solid compound (*cf.* hydrates of ammonia, p. 87). It has a strong smell resembling that of ammonia, and is a most penetrating reagent; it corrodes not only cork and indiarubber, but also glass.

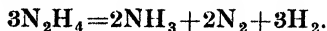
The solutions are oxidised by atmospheric oxygen:



They also decompose spontaneously, giving ammonia,<sup>6</sup> and more quickly in the presence of spongy platinum, giving nitrogen and hydrogen as well:



The spontaneous decomposition in the presence of a little alkali gives different proportions:



In connection with this instability it may be noted that the heat of formation in dilute solution (deduced from the heat of oxidation by  $\text{K}_2\text{Cr}_2\text{O}_7$ , etc.) is  $-9.5$  Cals.<sup>8</sup>

Hydrazine itself is obtained by distillation of the hydrate with anhydrous alkalies in a reducing atmosphere and under diminished pressure. Barium oxide may be used as alkali.<sup>5, 9</sup> The partly dehydrated base may be boiled with an excess of the oxide for three hours under a reflux condenser and then distilled in hydrogen at reduced pressure.

<sup>1</sup> Raschig, *Ber.*, 1907, 40, 4588.

<sup>2</sup> Raschig, *Chem. Zeit.*, 1907, 31, 926.

<sup>3</sup> Joyner, *Trans. Chem. Soc.*, 1923, 123, 1114.

<sup>4</sup> Curtius and Schultz, *J. prakt. Chem.*, 1890, [2], 42, 521.

<sup>5</sup> de Bruyn, *Rec. Trav. chim.*, 1894, 13, 433; 1895, 14, 83; 1896, 15, 174; 1899, 18, 297.

<sup>6</sup> Scott, *Trans. Chem. Soc.*, 1904, 85, 813.

<sup>7</sup> Tanatar, *Zeitsch. physikal. Chem.*, 1904, 40, 475; 1902, 41, 37.

<sup>8</sup> Berthelot and Matignon, *Ann. Chim. phys.*, 1892, [6], 27, 289; 1893, [6], 28, 138.

<sup>9</sup> Raschig, *Ber.*, 1910, 43, 1927; also Joyner, *Trans. Chem. Soc.*, 1923, 45, 188.

The product may contain 99.7 per cent. of hydrazine.<sup>1, 2</sup> It may also be prepared by a similar method from the carbonate or the borate.<sup>3</sup> The barium oxide may be replaced by solid sodium hydroxide.<sup>4</sup> The hydrochloride may be decomposed with sodium methoxide, and the methyl alcohol removed by distillation under diminished pressure.<sup>5</sup>

**Properties.**—Hydrazine is a colourless liquid which can easily be solidified; the solid melts at +1.4° C. The liquid boils at 113.5° C. under 761.5 mm., at 56° C. under 71 mm. pressure. The density is only slightly greater than that of water.  $D_4^{15}$  is 1.0114,<sup>5</sup> and  $D_4^{15}$  is 1.0258.<sup>6</sup>

The refractive index for the D line is 1.46979; for  $H_a$  it is 1.46675. The molecular refraction  $M_D$  is 8.867.<sup>3, 6</sup>

Hydrazine mixes in all proportions with water, with evolution of heat, 1.919 Cals. per mol. in dilute solution.<sup>7</sup>

It also mixes with some alcohols, but not with other organic solvents of the "normal" type, i.e. those which, on the evidence of many physical properties, appear to exist as simple molecules and are freely miscible with one another.

As a solvent it bears many resemblances to liquid ammonia. It dissolves sulphur and iodine, but with some chemical action.<sup>8</sup> Most of the sulphur is deposited again on pouring the solution into water, but some reacts with evolution of nitrogen and formation of an unstable hydrosulphide.<sup>8</sup> The alkali metals dissolve, and also react with evolution of hydrogen. Sodium gives a white explosive product,<sup>5</sup> which has been described as a derivative of azoimide,<sup>9</sup> or as a mono- or di-sodium hydrazate,  $NaN_2H_3$  and  $Na_2N_2H_2$ .<sup>10</sup> These solutions conduct electricity; nitrogen and hydrogen are evolved at the electrodes.<sup>1</sup> It also dissolves many salts, especially halides, nitrates, and ammonium salts. Typical solubilities are: NaCl, 12.2;  $KNO_3$ , 21.7; KI, 135.7;  $Ba(NO_3)_2$ , 81.1, in 100 parts by weight of hydrazine. All these solutions conduct electricity. Many reactions take place in this solvent. Thus, hydrazine sulphide and a zinc salt give zinc sulphide.

**Hydrazine as a Base.**—A solution of hydrazine in water reacts alkaline on account of electrolytic dissociation:



The constant of this dissociation is obtained from the following conductivity measurements:—

At V = 8	16	32	64	128	256
$\lambda = 1.4$	1.7	2.1	3.7	3.8	5.5
107k = 44	30	23	21	20	21 <sup>11</sup>

<sup>1</sup> Welsh, *J. Amer. Chem. Soc.*, 1915, 37, 497.

<sup>2</sup> Welsh and Broderick, *ibid.*, 1915, 37, 816, 825.

<sup>3</sup> Stollé, *Ber.*, 1904, 37, 4523.

<sup>4</sup> Raschig, *loc. cit.*

<sup>5</sup> de Bruyn, *loc. cit.*

<sup>6</sup> Bruhl, *Zeitsch. physikal. Chem.*, 1897, 22, 373.

<sup>7</sup> Bach, *ibid.*, 1892, 9, 241; 1893, 28, 138.

<sup>8</sup> Ephraim and Piotrowski, *Ber.*, 1911, 44, 386.

<sup>9</sup> Scandola, *Chem. Zentr.*, 1910, ii, 544.

<sup>10</sup> Schlenk and Weichselfelder, *Ber.*, 1915, 48, 669.

<sup>11</sup> Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 288.

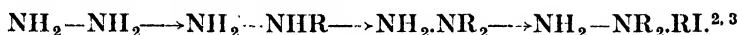


Assuming a kation mobility of 61, and that the mobility of the hydroxyl ion is 177 (both at 25° C.), the value of  $\lambda_0$  is 238, whence the dissociation constant is as stated in the third line. Taking into account the present accepted value of the mobility of OH', which is rather greater (*ca.* 190), the dissociation constant becomes  $2 \times 10^{-6}$  in round numbers; which is about  $\frac{1}{10}$  of the constant of ammonia (*q.v.*). The heat of neutralisation is also less than that of ammonia.

Thus the corresponding heats of formation of the salts in dilute solution are :<sup>1</sup>

$N_2H_4.HCl$ aq. . .	9·600 Cals.	$NH_4Cl$ aq. . .	12·390 Cals.
$N_2H_4.HNO_3$ aq. . .	9·700 „	$NH_4NO_3$ aq. . .	12·320 „
$N_2H_4 \cdot \frac{1}{2}H_2SO_4$ aq. . .	11·100 „	$\frac{1}{2}(NH_4)_2SO_4$ aq. . .	14·075 „

Although the salts of the diacid base are known in the solid state, they are completely dissociated in solution. Thus there is a difficulty in the addition of a hydron to the second  $-NH_2$ . This is no doubt connected with the fact that alkylation also only takes place on one  $-NH_2$ . The final product is a quaternary halide of the monacid base which cannot be alkylated further :



**Hydrazine as a Reducing Agent.**—Solutions of the free base and its salts are slowly oxidised by atmospheric oxygen. They are powerful reducing agents, and will reduce cupric and ferric salts to the cuprous and ferrous states, iodine to hydrogen iodide, and selenious acid to selenium. The noble metals are precipitated from their salts, and metallic copper is also similarly precipitated.

**Hydrazine Salts.**—Hydrazine combines with acids to form crystalline salts which in their composition show a formal similarity to the mono- and di-acid salts of a diacid base,  $N_2H_4.HX$  and  $N_2H_4.2HX$ . The evidence already mentioned, as well as that derived from the conductivity of these salts and the determinations of molecular weight in solution, renders it highly probable that the base is a monacid one, which is capable of forming acid salts (like ammonium bisulphate,  $NH_4HSO_4$ ) by evaporation with excess of acid.<sup>4,5</sup> The dihydrochloride,  $N_2H_4.2HCl$ , may be prepared by passing chlorine into an alcoholic solution of hydrazine hydrate :



It is also produced by precipitation of the sulphate with barium chloride. It may be crystallised from water in octahedra. The crystals melt at 180° C. with loss of HCl, and give the hydrochloride,  $N_2H_4.HCl$ . Aqueous solutions of the dihydrochloride are almost completely decomposed, giving one equivalent of free hydrochloric acid. This is proved by the velocity of inversion of cane sugar.<sup>1</sup>

Also the Van 't Hoff or activity coefficient "*i*" of a 0·5901N solution is 3·76, since nearly four ions are derived from one molecule, thus :

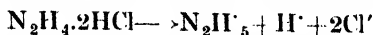
<sup>1</sup> Bach, *Zeitsch. physikal. Chem.*, 1892, 9, 241; 1893, 28, 138.

<sup>2</sup> Fischer, *Annalen*, 1877, 190, 102.

<sup>3</sup> Harries and Haga, *Ber.*, 1898, 31, 56.

<sup>4</sup> Curtius, *J. prakt. Chem.*, 1889, [2], 39, 27; 1890, [2], 42, 521; 1894, [2], 50, 275, 311, 508.

<sup>5</sup> Sabanejeff, *Zeitsch. anorg. Chem.*, 1898, 17, 480; 1899, 20, 21.



represents the dissociation as determined by the lowering of the freezing-point.

The densities of the solutions have been determined,<sup>1</sup> and also the refractivities.<sup>2</sup>

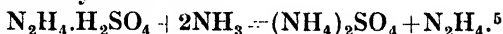
The monohydrochloride, ( $\text{N}_2\text{H}_4 \cdot \text{HCl}$ ), obtained from the di-salt by careful heating to  $140^\circ \text{C}$ ., crystallises from water in needles which melt at  $89^\circ \text{C}$ ., and on stronger heating decompose into  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$ .

The molar heat of solution is  $-5.440$  Cals., that of the acid salt, which includes the heat of dissociation, is  $-6.201$  Cals.<sup>2</sup>

The hydrobromide and hydriodide are made by similar methods. A salt,  $3\text{N}_2\text{H}_4 \cdot 2\text{HI}$ , is made by adding iodine to alcoholic hydrazine hydrate. The dihydrofluoride is made by direct combination in aqueous or aqueous alcoholic solution. It melts at  $105^\circ \text{C}$ ., and is more stable than the corresponding compounds with the other halogen hydric acids, since it sublimes without decomposition. In dilute solution the activity coefficient is about 2; it therefore gives only two ions, no doubt on account of the polymerisation of hydrofluoric acid, *i.e.*  $\text{N}_2\text{H}_5^+$  and  $\text{HF}'_2$ .

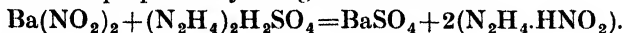
The disulphate, prepared by direct combination, crystallises in the form of tables or their prisms in the rhombic system. These melt with decomposition at  $254^\circ \text{C}$ . They are easily soluble in hot water, sparingly so in cold, and insoluble in alcohol. The activity coefficient in solutions containing 0.31 to 0.96 mols. to the litre is about 2. The molecule probably dissociates into  $\text{N}_2\text{H}_5^+$  and  $\text{HSO}'_4$ . The heat of solution of 1 mol. is  $-8.700$  Cals.<sup>3</sup>

The sulphate,  $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ , prepared from the calculated amounts of base and acid, may be precipitated by alcohol as an oil which becomes crystalline on rubbing.<sup>4</sup> The crystals melt at  $85^\circ \text{C}$ . The sulphates of hydrazine are decomposed by liquid ammonia, with liberation of the hydrazine. The reaction is quantitative, and may be used in preparing the anhydrous base:



The dinitrate,  $\text{N}_2\text{H}_4 \cdot 2\text{HNO}_3$ , is prepared from the sulphate and barium nitrate, and may be crystallised in deliquescent needles which melt with decomposition. The nitrate, obtained from nitric acid and the carbonate,<sup>6</sup> or by the addition of alcohol to a solution of the binitrate, may be crystallised in needles from hot alcohol. It is more stable than the binitrate, and may be heated far above its melting-point,  $69^\circ \text{C}$ ., without decomposition (*i.e.* to  $300^\circ \text{C}$ .).

The nitrite is prepared by the general reaction



The filtrate is concentrated *in vacuo* over  $\text{P}_2\text{O}_5$ , and may be crystallised from alcohol and ether. It decomposes on heating and explodes on percussion.



(See also under Nitrous Acid, p. 184.)

<sup>1</sup> Schiff and Mensacchi, *Zeitsch. physikal. Chem.*, 1896, 21, 292.

<sup>2</sup> Bach, *loc. cit.*

<sup>3</sup> Berthelot and Matignon, *loc. cit.*

<sup>4</sup> Curtius, *J. prakt. Chem.*, 1891, 44, 101.

<sup>5</sup> Browne and Welsh, *J. Amer. Chem. Soc.*, 1911, 33, 1728.

<sup>6</sup> Curtius and Jay, *J. prakt. Chem.*, 1889, [2], 39, 27, 107.

<sup>7</sup> Sommer, *Zeitsch. anorg. Chem.*, 1913, 83, 119.

Hydrazine forms a series of double salts with salts of metals, which resemble to some extent the corresponding ammonium double salts.<sup>1</sup> Zinc hydrazine chloride,  $\text{ZnCl}_2 \cdot 2\text{N}_2\text{H}_4 \cdot \text{HCl}$ , crystallises in needles; it is soluble in alcohol. Double chlorides are also formed with the chlorides of cadmium, mercury, and tin. The platinichloride,  $2\text{N}_2\text{H}_5 \cdot \text{HCl} \cdot \text{PtCl}_4$ , is obtained as a yellow precipitate from a concentrated aqueous alcoholic solution.<sup>2</sup>

The double sulphates differ from those of ammonia by crystallising anhydrous and being less soluble in water. Those of zinc and nickel have the composition  $\text{ZnSO}_4 \cdot (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$  and  $\text{NiSO}_4 \cdot (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ .

By the addition of hydrazine hydrate to salt solutions, addition compounds or hydrazinates corresponding to amines are precipitated,<sup>1,3</sup> e.g.  $\text{NiSO}_4 \cdot 8\text{N}_2\text{H}_4$ ,  $\text{ZnCl}_2 \cdot 2\text{N}_2\text{H}_4$ . Compounds of this type are formed also by salts of Co, Cd, Cu, and Hg, but not by those of manganese, iron, copper, and tin.

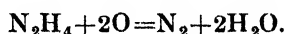
**Derivatives of Hydrazine.**—In addition to the numerous organic derivatives in which the hydrogen is replaced by alkyl or aryl radicals, etc., there are a few derivatives of inorganic acids, but these also are more stable if some of the hydrogen is replaced by organic radicals.

The sulphonate,  $\text{H}_2\text{N}-\text{NH}-\text{SO}_3\text{H}$ , and the disulphonate are known.<sup>4</sup> When air is passed through fuming sulphuric acid and then through anhydrous hydrazine, hydrazine hydrazine-sulphonate is produced:



Among the carboxyl and carbonyl substitution products are hydrazine-carboxylic acid,  $\text{NH}_2-\text{NH}-\text{COOH}$ , the dicarboxylic acid,  $\text{HOOC}-\text{NH}-\text{NH}-\text{COOH}$ , carbonic-acid dihydrazide,  $\text{CO}(\text{NH} \cdot \text{NH}_2)_2$ , and the amide hydrazide or semi-carbazide,  $\text{NH}_2-\text{CO}-\text{NH} \cdot \text{NH}_2$ .

**Detection and Estimation.**—The reactions which are used in the analysis of hydrazine and its salts usually depend upon its oxidation. Thus it is determined by titration with potassium permanganate in acid solution,<sup>6</sup> or with vanadic acid.<sup>7</sup> Nitrogen is quantitatively evolved:



Hydrazine is also a useful reagent in general analysis. A solution made by dissolving the hydrochloride in an excess of alkali will quantitatively precipitate copper as metal. The copper solution is added drop by drop. Copper can be estimated in this way in the presence of tin zinc.<sup>8</sup>

Hydrazine alone does not reduce chlorates, bromates, or iodates, but in the presence of cupric oxide the reduction is quantitative:



The chloride, etc., may then be determined in the usual manner after decomposition of the excess of hydrazine with permanganate and nitric acid.<sup>9</sup>

<sup>1</sup> Curtius and Schrader, *J. prakt. Chem.*, 1894, 50, 311.

<sup>2</sup> Thiele, *Annalen*, 1892, 270, 33.

<sup>3</sup> Hofmann and Marburg, *ibid.*, 1899, 305, 191.

<sup>4</sup> Stollé, *Ber.*, 1899, 30, 799; 1904, 37, 4523.

<sup>5</sup> Traube and Vockerodt, *ibid.*, 1914, 47, 938.

<sup>6</sup> Petersen, *Zeitsch. anorg. Chem.*, 1894, 5, 1.

<sup>7</sup> Hofmann and Kisspert, *Ber.*, 1898, 31, 64.

<sup>8</sup> Jannasch and Biedermann, *ibid.*, 1900, 33, 631.

<sup>9</sup> Hodgkinson, *J. Soc. Chem. Ind.*, 1914, 13, 815.

THE SULPHONIC AND SULPHINIC SUBSTITUTION PRODUCTS OF  
AMMONIA, HYDROXYLAMINE, AND HYDRAZINE.

These compounds may also be regarded as derivatives of sulphurous and sulphuric acids, and as such are included in Vol. VII. of this series. Some accounts have already been given under Ammonia, and the derivatives of hydroxylamine and hydrazine have been described with these compounds.

This description is summarised in the following conspectus, which includes those compounds which are known in the pure state or in solution, or as salts. Some further notes on the ammonia derivatives are added.

Amido-sulphinic Acids.

Thionyl amide	}	. . .	NH <sub>2</sub> —SO—NH <sub>2</sub> .
Diamide of sulphurous acid			
Amido-sulphinic acid	. . .	NH <sub>2</sub> —SO—OH.	
Imido-disulphinic acid	. . .	NH—(SO—OH) <sub>2</sub> .	
Imido-disulphamide	. . .	NH(SO <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> .	
Nitrilo-trisulphuric acid	. . .	N(SO <sub>2</sub> H) <sub>3</sub> .	
Ammonium amido-sulphinate	. . .	NH <sub>2</sub> —SO <sub>2</sub> NH <sub>4</sub> ,	
or			
Sulphuryl diammine	. . .	SO <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> .	
Diammonium imido-disulphinate	. . .	NH(SO <sub>2</sub> NH <sub>4</sub> ) <sub>2</sub> .	
Triammonium imido-disulphinate	. . .	NH <sub>4</sub> —N(SO <sub>2</sub> NH <sub>4</sub> ) <sub>2</sub> .	

Amido-sulphonic Acids.

Sulphuryl amide	}	. . .	$\text{NH}_2\text{—SO}_2\text{—NH}_2.$
Diamide of sulphuric acid			
Amido-sulphonic acid	. . .	$\text{NH}_2\text{—SO}_2\text{—OH.}$	
Imido-disulphonic acid	. . .	$\text{NH—(SO}_3\text{H)}_2.$	
Nitrilo-trisulphonic acid	. . .	$\text{N(SO}_3\text{H)}_3.$	
Trisulphimide	. . .	$(\text{NH=SO}_2)_3$ (cyclic).	
Imido-disulphonamide	. . .	$\text{NH(SO}_2\text{NH}_2)_2.$	

Hydroxylamine Sulphonic Acids.

Hydroxylamine $\alpha$ -sulphonic acid	}	. . .	$\text{NH}_2\text{—O—SO}_3\text{H.}$
or			
Amido-persulphuric acid			$\text{HO—HN—SO}_3\text{H.}$
Hydroxylamine $\beta$ -sulphonic acid			$\text{HO}_3\text{S—O—NH—SO}_3\text{H.}$
Hydroxylamine $\alpha\beta$ -disulphonic acid			$\text{HO—N}=(\text{SO}_3\text{H})_2.$
Hydroxylamine $\beta\beta$ -disulphonic acid			$\text{HO}_3\text{S—O—N}=(\text{SO}_3\text{H})_2.$
Hydroxylamine $\alpha\beta\beta$ -trisulphonic acid			$\text{HO}_3\text{S—O—N}=(\text{SO}_3\text{H})_2.$

Hydrazine Sulphonic Acids.

Hydrazine sulphonic acid	. . .	NH <sub>2</sub> —NH—SO <sub>3</sub> H.
Hydrazine symmetrical disulphonic acid	. . .	HO <sub>3</sub> S—NH—NH—SO <sub>3</sub> H.

**Sulphinic Derivatives.**—The action of dry SO<sub>2</sub> on dry NH<sub>3</sub> produces a variety of coloured compounds having the empirical formulæ (NH<sub>3</sub>)<sub>x</sub>(SO<sub>2</sub>)<sub>y</sub>.<sup>1, 2, 3</sup> It appears, however, that a little water is required

<sup>1</sup> Döbereiner, *Schweigger's J.*, 1826, 47, 120.

<sup>2</sup> Rose, *Annalen*, 1834, 33, 235; 1837, 42, 415; 1844, 61, 397.

<sup>3</sup> Schumann, *Zeitsch. anorg. Chem.*, 1900, 23, 43.

in order that combination may occur freely. In ethereal dry solution a compound,  $(\text{NH}_3)_2\text{SO}_2$ , has been isolated as a white solid, which may also be the ammonium salt of amido-sulphinic acid.<sup>1</sup>

Organic substitution products of amino-sulphinic acid,  $\text{R}-\text{NH}-\text{SO}_2\text{H}$ , and of thionyl imide,  $\text{R}-\text{N}=\text{SO}$ , are known.

The addition of thionyl chloride drop by drop to liquid ammonia gives a red solution, from which triammonium imido-disulphinate can be isolated. This may also be formed by the hydrolysis of imido-sulphonamide.<sup>2</sup>

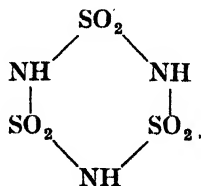
**Sulphonic Derivatives.**—The reaction between sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ , and dry ammonia gives under various conditions sulphamides and sulphimides. Some of these products were early prepared in an impure state.<sup>3, 4</sup>

In ligroin solution, trisulphimide (see table), sulphomelide (*vide infra*), and sulphamide are present. After removal of chloride with  $\text{PbO}$ , the silver salts of these compounds are precipitated in the order given, the last being that of sulphamide, which is then decomposed with the theoretical amount of  $\text{HCl}$ . The free sulphamide is recrystallised from hot alcohol.<sup>5</sup> Or, the compound may be prepared in chloroform solution, the solvent then distilled, and the residue, dried at  $100^\circ \text{C}$ ., is mixed with sand and extracted with ethyl acetate.<sup>6</sup>

An entirely different method of making sulphamide by the decomposition of ammonium amido-sulphite has also been described.<sup>1</sup>

The compound crystallises in colourless rhombic tables, melting at  $91.5^\circ$  to  $93^\circ \text{C}$ ., easily soluble in cold water, hot methyl, or ethyl alcohols.

The molar weight in water corresponds to the formula  $\text{SO}_2\cdot\text{N}_2\text{H}_4$ . At  $100^\circ \text{C}$ . it is decomposed with evolution of ammonia. In solution it is hydrolysed by acids to ammonium sulphate, by alkalies less completely, to salts of amido-sulphonic acid. The aqueous solution does not react acid or conduct the electric current, but the hydrogen, while not ionised in solution, can be displaced with formation of salts. Thus the insoluble silver salt is precipitated by double decomposition. Mono- and di-potassium salts,  $\text{SO}_2\text{N}_2\text{H}_3\text{K}$  and  $\text{SO}_2\text{N}_2\text{H}_2\text{K}_2$ , are obtained by the reaction between the compound and potassium amide in liquid ammonia.<sup>7</sup> Trisulphimide,  $(\text{SO}_2\text{NH})_3$ , as a silver salt is the first fraction of the precipitate mentioned above. Esters are also known, but the free compound has only been prepared in solution. It is considered to have the formula



analogous to that of cyanuric acid,  $(\text{OCNH})_3$ .<sup>5</sup>

<sup>1</sup> Divers and Ogawa, *Trans. Chem. Soc.*, 1900, 77, 327; 1901, 79, 1099; 1902, 81, 504.

<sup>2</sup> Ephraim and Pietrowski, *Ber.*, 1911, 44, 379. See also Ephraim and Garewitsch, *ibid.*, 1910, 43, 138.

<sup>3</sup> Regnault, *Ann. Chim. Phys.*, 1838, [2], 69, 170.

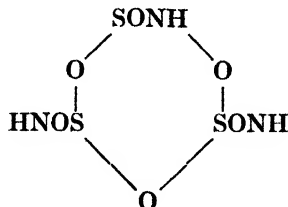
<sup>4</sup> Traube, *ibid.*, 1893, 26, 607.

<sup>5</sup> Hantzsch and Holl, *ibid.*, 1901, 34, 3430.

<sup>6</sup> Ruff, *Ber.*, 1903, 36, 2900.

<sup>7</sup> Franklin and Stafford, *Amer. Chem. J.*, 1902, 28, 83.

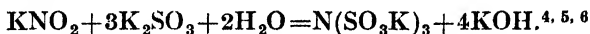
The ammonium salt of an isomeric compound,  $(\text{SO}_2\text{NH})_3$ , is present in the residues after the distillation of ligroin from the products of the reaction which occurs between  $\text{SO}_2$  and  $\text{NH}_3$ . The structure is said to be cyclic,



and analogous to that of cyamelide.<sup>1</sup>

Imido-sulphamide (see table) is formed when the silver salt of trisulphimide is treated with  $\text{H}_2\text{S}$ . It appears as colourless crystals, melting at  $160^\circ \text{C}$ ., which are soluble in ether, and in water, giving an acid solution from which ammonium, alkali, and silver salts can be obtained by displacement of the imino-hydrogen.<sup>2, 1</sup> It is also made from ammonium carbamate and pyrosulphuryl chloride.<sup>3</sup>

Nitrilo-sulphonic acid or amino-trisulphonate,  $\text{N}(\text{SO}_3\text{H})_3$ , has long been known in the form of its potassium salt, which is precipitated as crystals when a mixture of 1 mol. of  $\text{KNO}_2$  and 3 mols. of  $\text{K}_2\text{SO}_3$  is allowed to stand:



The sodium salt is formed when  $\text{SO}_2$  is passed into a fairly concentrated solution containing 2 mols. of  $\text{NaNO}_2$  and 3 mols. of  $\text{Na}_2\text{CO}_3$ .<sup>7</sup>

It differs from the potassium salt in being more soluble and in crystallising with 5 mols. of water instead of with 2. These salts are hydrolysed quickly into the imido-, more slowly into the amido-, salts, especially in acid solution. Disodium imido-disulphonate is prepared by expelling the  $\text{SO}_2$  from the above-mentioned sodium nitrilo-sulphonate by a current of air. The solution is then made slightly alkaline with  $\text{Na}_2\text{CO}_3$  and evaporated. Sodium sulphate crystallises first, and then  $\text{NII}(\text{SO}_3\text{Na})_2$ .

#### AZOIMIDE.

**Historical.**—Organic compounds containing three or four atoms of nitrogen united to one another (the triazo- and tetrazo-compounds) are numerous and often stable. Thus diazo-amido-compounds,  $\text{RN}=\text{N}-\text{N}-\text{NHR}$ , contain the triazene group. Compounds containing the cyclic triazene group or azide ring,



<sup>1</sup> Hantzsch and Stuer, *Ber.*, 1905, 38, 1022.

<sup>2</sup> Hantzsch and Holl, *loc. cit.*

<sup>3</sup> Mente, *Annalen*, 1888, 248, 232.

<sup>4</sup> Claus, *ibid.*, 1869, 152, 336; 1871, 158, 52, 194.

<sup>5</sup> Fremy, *Ann. Chim. Phys.*, 1845, [3], 15, 408.

<sup>6</sup> Berglund, *Ber.*, 1876, 9, 252.

<sup>7</sup> Divers and Haga, *Trans. Chem. Soc.*, 1901, 29, 1903; 1893, 61, 943; 1896, 69, 1620.



The aqueous solution reacts acid. Its conductivity, determined at concentrations of from 0.1 to 0.001N, gives a mean dissociation constant of about  $1.8 \times 10^{-5}$ . This increases somewhat with increase of concentration, resembling in this respect the constant of a stronger acid.<sup>1</sup>

Solutions containing rather less than 30 per cent. of the acid give off its vapour, which produces dense fumes of ammonium azide when brought into contact with ammonia vapour. The vapour of hydrazoic acid has a most unpleasant smell, and causes inflammation of the mucous membrane when inhaled. The solution is poisonous and attacks the skin. Even in small quantities (0.1 per cent.) it is poisonous to plants, and will prevent the germination of seedlings.<sup>2</sup>

Although the solution is fairly stable, yet on long boiling with mineral acids it is decomposed into nitrogen and ammonium salts, a decomposition which is much accelerated by the presence of platinum black.<sup>2</sup>

When the solution is electrolysed hydrogen is evolved at the cathode, and nitrogen, probably by a secondary oxidation of the compound (as in the case of solutions of ammonia), at the anode.<sup>3,4</sup> Strong oxidising agents such as potassium permanganate convert it into water and nitrogen.

With nitrous acid, hydrazoic acid gives nitrous oxide in addition to nitrogen:



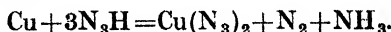
It is easily reduced by sodium amalgam, by zinc and acid, by ferrous hydroxide, etc., to ammonia and hydrazine:



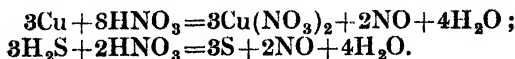
It is also reduced by polysulphides or  $\text{H}_2\text{S}$ :



Hydrazoic acid dissolves the more electro-positive metals, magnesium, aluminium, zinc, and iron, with evolution of hydrogen in most cases. The nascent hydrogen is partly, or it may be wholly, used to reduce the hydrazoic acid to ammonia. Thus in the case of copper no hydrogen is set free:



In several of its reactions hydrazoic acid shows a similarity to nitric acid, as is seen by comparing the corresponding reactions with copper and hydrogen sulphide:



**Salts of Hydrazoic Acid.**—The azides of many metals have been prepared in the crystalline state. In these the acid is always monobasic; the formulæ therefore correspond to those of the halides, and the properties are often intermediate between those of a chloride and of a bromide.

<sup>1</sup> West, *Trans. Chem. Soc.*, 1900, 77, 705.

<sup>2</sup> Löw, *Ber.*, 1891, 24, 2947.

<sup>3</sup> Peratoner and Oddo, *Gazzetta*, 1895, 25, ii, 13.

<sup>4</sup> Szarvasy, *Trans. Chem. Soc.*, 1900, 77, 603.



The azides of the alkalis,  $\text{LiN}_3$ ,  $\text{NaN}_3$ ,  $\text{KN}_3$ , and  $\text{NH}_4\text{N}_3$ , are easily soluble in water and also soluble in alcohol. Those of the alkaline earths, namely,  $\text{MgN}_6$ ,  $\text{CaN}_6$ , etc., are also soluble. Other azides, such as  $\text{CuN}_6$  (red-brown),  $\text{AgN}_3$  (white),  $\text{HgN}_3$  and  $\text{HgN}_6$ ,  $\text{PbN}_6$  and  $\text{TiN}_3$ , are sparingly soluble or almost insoluble in water. The remaining metals mostly give basic salts.<sup>1, 2, 3, 4, 5, 6</sup>

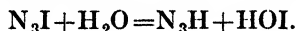
Lead azide is well known as a detonator, and is used in the fuses of shells.

The formulae of many salts have been proved by the electrolysis of solutions of  $\text{NH}_4\text{N}_3$  in liquid ammonia.<sup>7</sup>

The azides of the alkali and alkaline earth metals are not explosive, and some may even be melted without decomposition. The azides of Na, K, Rb, and Cs give up their nitrogen quietly at about  $300^\circ$  to  $350^\circ$  C.; those of Ca, Sr, Ba do so at about  $100^\circ$  to  $120^\circ$  C. Consequently they have been used as a source of pure nitrogen.<sup>8</sup>

A few double salts have been prepared, compounds of alkali azides with those of other metals, chiefly belonging to Group VIII., e.g.  $\text{NH}_4\text{N}_3 \cdot \text{CoN}_6$  (blue), are known.

**Azides of the Halogens.**—*Iodine Azide.*—This compound has been prepared by bringing an aqueous suspension of silver azide into contact with an ethereal solution of iodine.<sup>9</sup> On evaporation of the ether in a current of air, colourless crystals are left which have a penetrating odour similar to that of cyanogen iodide, and which are easily decomposed by explosion into iodine and nitrogen. The compound may be hydrolysed by water, giving azoimide and hypiodous acid :



The iodine is therefore the electro-positive part of the molecule.

*Bromine Azide* has also been prepared by the action of bromine vapour on sodium or silver azide. It is very explosive even at low temperatures.<sup>10</sup>

*Chlorazide* may be made by acidifying a solution containing sodium azide and hypochlorite by a weak acid such as boric. It is a colourless gas, smelling like hypochlorous acid. In alkaline solution it is rapidly hydrolysed to its generators, the reaction proceeding from left to right :



The gas easily explodes with great violence and the appearance of blue flames.<sup>11</sup>

**Constitution.**—The constitution of organic compounds containing the azide ring is established by the consideration of their preparations and reactions, on the assumption that the usual valencies are exerted

<sup>1</sup> Curtius, *loc. cit.*

<sup>2</sup> Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 261.

<sup>3</sup> Curtius and Darapsky, *ibid.*, 1900, [2], 61, 408.

<sup>4</sup> Dennis and Doan, *J. Amer. Chem. Soc.*, 1896, 18, 970.

<sup>5</sup> Dennis and Benedikt, *Zeitsch. anorg. Chem.*, 1898, 17, 18.

<sup>6</sup> Berthelot and Vieille, *Bull. Soc. chim.*, 1895, [3], 11, 744.

<sup>7</sup> Browne, Holmes, and King, *J. Amer. Chem. Soc.*, 1919, 41, 1769.

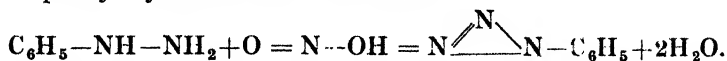
<sup>8</sup> Tiede, *Ber.*, 1916, 49, 1742.

<sup>9</sup> Hantzsch, *ibid.*, 1900, 33, 522.

<sup>10</sup> Spencer, *Trans. Chem. Soc.*, 1925, 127, 216.

<sup>11</sup> Raschig, *Ber.*, 1908, 41, 4194.

by the elements involved. Thus phenyl azide is made by the condensation of phenyl hydrazine and nitrous acid:



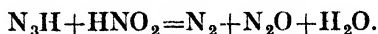
The analogous reaction between hydrazine itself and nitrous acid (*vide supra*) leads to an analogous formula for the hydrogen compound, which also agrees well with the other reactions used in its preparation. Azoinide is unique in being the only compound containing one atom of hydrogen united with more than one atom of a second element. It is so extremely improbable that the atomic weight of hydrogen should be divided by three on this account, that preferably the univalency of the group  $\text{N}_3\text{--}$  is assumed and accounted for by the cyclic formula.

**Detection and Estimation.**—The compound may easily be recognised by the highly characteristic properties and reactions mentioned above. In solution it gives precipitates with silver salts, as halides do, but may be distinguished from chloride and bromide by means of the brown precipitate of the cupric salt. Another distinctive test is an intense red colour with ferric salts, ( $\text{FeN}_3$ ). The evolution of nitrogen when it is oxidised by iodine, etc. (*vide infra*), also serves to distinguish it from halides as well as from thiocyanates.

The quantitative analysis depends on oxidation with iodine or nitrous acid.<sup>1</sup> A neutral or alkaline solution is mixed with a slight excess of iodine solution and a crystal of sodium thiosulphate added, which hastens the evolution of nitrogen. In very dilute solutions ceric nitrate or sulphate should be added.

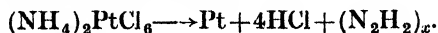
The reaction between an azide and nitrous acid is quantitative, and may be used to estimate the latter (see Nitrous Acid, p. 184).

A measured excess of the azide is added to the acidified nitrite solution. After shaking for a few minutes the mixture is made alkaline with baryta, and is boiled to expel the gases. It is then acidified with acetic acid, and the excess of azoinide titrated with iodine and thio-sulphate,



Azides may also be estimated as nitrogen after decomposition with ceric ammonium nitrate in a nitrometer.<sup>2</sup>

**Di-imide,  $(\text{N}_2\text{H}_2)_x$ ,** a gaseous substance, is said to be formed when ammonium platinichloride is heated:



#### SUMMARY OF THE HYDRIDES OF NITROGEN.

The list of compounds or ions containing nitrogen and hydrogen alone is as follows:—

$\text{NH}_4^+$ Ammonium	$\text{NH}_3$ Ammonia	$\text{N}_2\text{H}^+$ Hydrazonium	$\text{N}_2\text{H}_4$ Hydrazine
$(\text{N}_2\text{H}_2)$ Di-imide	$\text{N}_4\text{H}_4$ Ammonium azide	$\text{N}_5\text{H}_5$ Hydrazine azide	$\text{N}_3\text{H}$ Azoimide

<sup>1</sup> Raschig, *Chem. Zeit.*, 1908, 32, 1203.

<sup>2</sup> Copeman, *J. S. African Chem. Inst.*, 1927, 10, 18.

which can all be regarded as built up of the amino  $\text{—NH}_2$  and azide  $\text{—N}_3$  radicals in various combinations with hydrogen, hydrogen-ion  $\text{H}^+$ , and one another.

One of the hydrogen atoms in the hydrides ammonia and possibly hydrazine, is of a sufficiently acidic character to be replaced by an alkali metal; but in spite of the electro-negative position of nitrogen in the periodic table, the enhancement of electro-negative character conferred by the azide ring is required in order that a hydrogen may be ionised in solution.

The reducing power or ease of oxidation reaches its maximum in the case of hydrazine, and is less in the case of the more highly hydrogenated ammonia, which resists atmospheric oxidation in the cold, as also the effect of mild oxidising agents in solution. The greater stability of azoimide towards oxidising agents is partly due to the stability of the cyclic structure, and is also intelligible on the grounds that it is already the most highly oxidised compound of nitrogen and hydrogen, as is experimentally proved by the products of its reduction with sodium amalgam, as also by the method of its preparation. Generally, the order of hydrogenation as shown above agrees with such reactions as the oxidation of ammonia to hydrazine by hypochlorites, and of hydrazine to azoimide by nitrous acid (see pp. 124, 182).

The three primary hydrides,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ , and  $\text{N}_3\text{H}$ , all have a strong affinity for water, with which they mix in all proportions, and all three solutions probably contain hydrates.

Pure liquid ammonia and hydrazine have a strong resemblance to water in some physical properties, as well as in their properties as solvents. Hydrogen trinitride resembles hydrogen chloride in its salts, while in its reduction by nascent hydrogen, *e.g.* when it acts on metals, it resembles nitric acid.

#### OXYGEN AND HYDROXYL SUBSTITUTION PRODUCTS OF HYDRAZINE.

These compounds are chiefly represented by organic derivatives, namely,  $\text{RN} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{NR}$  (azoxy-compounds),  $\text{R—N=NOH}$  (free diazo-compounds),  $\text{R—NH—NO}$  (their tautomeric forms, nitrosamines),  $\text{RH=N—NO}_2$  and  $\text{R}_2\text{N=N—NO}_2$  (nitramines).

Although dinitrous acid, or rather dinitronic acid,  $(\text{HO—NO})_2$ , does not exist, the intermediate oxidation products of hydrazine, namely,  $\text{H}_2\text{N—NO}_2$ , nitramide,  $\text{HO—N—NOH}$ , hyponitrous acid and nitrohydroxylamine,  $\text{HO—NH—NO}_2$ , have been prepared.

**Nitramide**,  $\text{H}_2\text{N—NO}_2$  or  $\text{HO—NH—NO}$ .—This compound is prepared by splitting off the organic radicals from some nitramines,  $\text{R}_2\text{N—NO}_2$ .<sup>1</sup> Nitrourethane,  $\text{NO}_2\text{—NH—CO—OC}_2\text{H}_5$ , is treated with ammonia in ethereal solution, the ammonium salt is decomposed with potassium hydroxide in methyl alcohol, the precipitated potassium salt is washed with alcohol and dried in a desiccator. It is then hydrolysed with a mixture of ice and some concentrated sulphuric acid:

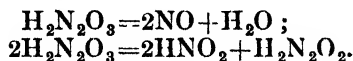


<sup>1</sup> Thiele and Lachmann, *Annalen*, 1895, 288, 267.

It is a white crystalline solid, soluble in water, alcohol, and ether, but not in hydrocarbons. It melts with decomposition above  $72^{\circ}\text{C}$ . The molecular weight in water is 61.<sup>1</sup> The solution reacts slightly acid, but the degree of dissociation as determined by conductivity measurements is very low.<sup>2</sup>

It is instantly decomposed by alkalis, giving  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ . Salts are unknown, with the exception of the mercuric salt,  $\text{HgN}_2\text{O}_2$ .

**Nitrohydroxylamine**,  $\text{HO}-\text{NH}-\text{NO}_2$  or  $\text{HO}-\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{N}-\text{OH}$ , is obtained in the form of salts by the action of ethyl nitrate on alcoholic hydroxylamine.<sup>3</sup> When the salts, *e.g.*  $\text{Na}_2\text{N}_2\text{O}_3$ , are acidified, the free acid instantly decomposes into nitric oxide and water, or nitrous and hyponitrous acids:



The sodium salt, made by the above reaction in methyl alcohol, is a white powder, soluble and deliquescent. It absorbs oxygen from the air, giving  $\text{NaNO}_2$  and  $\text{NaNO}_3$ . The aqueous solution when boiled decomposes into nitrite and nitrous oxide:



The salts of the calcium group, *e.g.*  $\text{CaN}_2\text{O}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , are sparingly soluble. The silver salt is almost insoluble. Salts of cadmium and mercury have also been prepared.<sup>4, 5</sup>

A great number of organic derivatives of the above are known under the name of diazo-compounds, as well as derivatives of compounds which have not yet been prepared in the free state, such as  $\text{R.N}_2\text{O}_2\text{H}$ , derived from nitrosohydroxylamine,  $\text{HO}-\text{NH}-\text{NO}$ , which is isomeric with nitranide.<sup>6, 7, 8, 9</sup>

<sup>1</sup> Hantzsch and Kaufmann, *Annalen*, 1892, 292, 317.

<sup>2</sup> Baur, *ibid.*, 1897, 296, 95.

<sup>3</sup> Angeh, *Gazzetta*, 1896, 26, ii, 17; 1897, 27, ii, 357.

<sup>4</sup> Angeli and Angelico, *ibid.*, 1900, 30, 1.

<sup>5</sup> Angelico and Fanara, *ibid.*, 1901, 31, ii, 15.

<sup>6</sup> Thiele, *Annalen*, 1895, 288, 269.

<sup>7</sup> Hantzsch, *ibid.*, 1898, 299, 67.

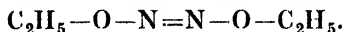
<sup>8</sup> Traube, *ibid.*, 1898, 300, 81.

<sup>9</sup> Angeli and Angelico, *Gazzetta*, 1903, 33, ii, 239.

## CHAPTER IX.

### HYPONITROUS ACID.

**Historical.**—It was shown by Divers in 1871<sup>1, 2</sup> that the reduction of sodium nitrate with sodium amalgam gave a salt having the empirical composition  $\text{NaNO}$ , the acid being an isomer of nitramide. This salt can also be prepared by electrolytic reduction of a nitrite. The reactions of the ethyl ester showed that this is constituted as a diazo-compound :



The ester reacts with water, giving  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{N}_2$ .<sup>3</sup>

A bibliography of hyponitrous acid has been compiled by Divers,<sup>4</sup> to whose researches so much of our knowledge of this interesting compound is due.

**Methods of Preparation of Hyponitrites.**—Four general methods of preparation are known, under which numerous special methods may be classified. There are also a few other methods of subsidiary importance.

1. By the reduction of nitrites.
2. By the action of nitrous acid on hydroxylamine (or oxidation of hydroxylamine).
3. By the alkaline hydrolysis of hydroxylamine sulphonates.
4. By the hydrolysis of some organic compounds containing the diazo-group.

1. The reduction of sodium or potassium nitrite by sodium amalgam proceeds according to the equation



The amalgam is added to the nitrite in the ratio 4Na to 1 $\text{KNO}_2$ . The solution is kept cold. When the gas evolution ceases, the solution is neutralised by acetic acid and silver nitrate is added. The precipitate of yellow  $\text{Ag}_2\text{N}_2\text{O}_2$  is washed in the dark with cold water, dissolved in cold dilute nitric acid, and reprecipitated with sodium carbonate solution. The purified  $\text{Ag}_2\text{N}_2\text{O}_2$  is again washed and dried *in vacuo* over concentrated sulphuric acid. The yield is not good.

Or,  $\text{Ba}(\text{NO}_2)_2$  may be reduced with sodium amalgam, and the  $\text{Ag}_2\text{N}_2\text{O}_2$  precipitated as above.<sup>3</sup>

2. Ferrous hydroxide will also reduce nitrates to hyponitrites. Pure ferrous sulphate is precipitated with milk of lime, and to the cooled

<sup>1</sup> Divers, *Proc. Roy. Soc.*, 1871, 19, 425.

<sup>2</sup> Maumené, *Compt. rend.*, 1870, 70, 146.

<sup>3</sup> Zorn, *Ber.*, 1870, 12, 1509.

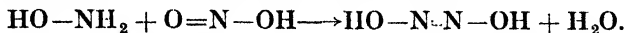
<sup>4</sup> Divers, *Trans. Chem. Soc.*, 1899, 75, 97.

<sup>5</sup> Divers and Haga, *ibid.*, 1889, 55, 760.

<sup>6</sup> Divers and Haga, *ibid.*, 1899, 75, 77.

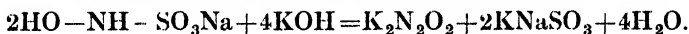
mixture is added 1 mol. of  $\text{NaNO}_3$  for each 10 mols. of  $\text{FeSO}_4$ . The hyponitrite is precipitated with silver nitrate.<sup>1</sup>

A solution of  $\text{NaNO}_2$  is added to a solution of  $\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$ . The mixture is heated quickly to  $60^\circ \text{C}$ . and  $\text{AgNO}_3$  is added at once. This method does not give good yields, but it proves that hyponitrous acid is a dioxime.<sup>2, 3, 4, 5</sup> It proceeds as follows:—

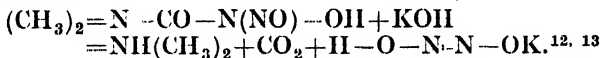


Hyponitrous acid has also been prepared by the oxidation of hydroxylamine with  $\text{CuO}$ ,  $\text{HgO}$ ,  $\text{Ag}_2\text{O}$ ,<sup>6</sup> and by the oxidation of hydroxylamine with  $\text{N}_2\text{O}_3$  in methyl-alcoholic solution.<sup>7</sup>

3. The most serviceable method of preparation is that which proceeds from the interaction of sulphites and nitrites. The potassium salt of hydroxylamine  $\beta\beta$ -disulphonic acid, prepared as described above (p. 108), is partly hydrolysed by hot water, giving potassium bisulphate and the potassium salt of the  $\beta$ -mono-sulphonic acid, *i.e.*  $\text{HO}-\text{NH}-\text{SO}_3\text{K}$ . When this salt is fused with alkalis and the melt dissolved in water, the hyponitrite may be precipitated by silver nitrate as the silver salt, or, by the addition of a large excess of alcohol, the alkali hyponitrite may be separated from the excess of alkali and hydroxylamine. The yield may be 60 per cent. of the theoretical: <sup>8, 9, 10, 11</sup>



4. The alkaline hydrolysis of organic substitution products of nitroso-hydroxylamine gives, by intramolecular change, salts of the tautomeric hyponitrous acid:



Further directions and improvements in these methods of preparation have been described.<sup>14</sup>

**Properties of Hyponitrites.**—The normal alkali salts of the dibasic acid are soluble in water, and are hydrolysed, giving alkaline solutions. Normal salts of other bases are very slightly soluble. The acid salts are very unstable, like the free acid. Silver hyponitrite is a yellow amorphous substance, non-hygroscopic, which may be boiled in water without decomposition. In the dry state it decomposes at  $100^\circ \text{C}$ ., giving  $\text{AgNO}_3$ , and it explodes at  $150^\circ \text{C}$ . It dissolves in nitric acid, and is reprecipitated by alkalis. Acetic acid and hydrogen sulphide set free hyponitrous acid. It is decomposed by hot alkalis. It reacts with alkyl iodides, giving alkyl hyponitrites.

<sup>1</sup> Dunstan and Dymond, *Trans. Chem. Soc.*, 1887, 51, 646.

<sup>2</sup> Wislicenus, *Ber.*, 1893, 26, 772.

<sup>3</sup> Paal, *ibid.*, 1893, 26, 1026.

<sup>4</sup> Thum, *Monatsh.*, 1893, 14, 294.

<sup>5</sup> Tanatar, *Ber.*, 1894, 27, 187.

<sup>6</sup> Hantzsch and Kaufmann, *Annalen*, 1896, 292, 317.

<sup>7</sup> Kaufmann, *ibid.*, 1898, 299, 98.

<sup>8</sup> Divers and Haga, *Trans. Chem. Soc.*, 1889, 55, 760.

<sup>9</sup> Divers and Haga, *ibid.*, 1899, 75, 77.

<sup>10</sup> Rây, De, and Dhar, *J. Chem. Soc.*, 1913, 103, ii, 1562.

<sup>11</sup> Kirschner, *Zeitsch. anorg. Chem.*, 1898, 16, 424.

<sup>12</sup> Hantzsch and Sauer, *Annalen*, 1898, 299, 89.

<sup>13</sup> Wieland, *ibid.*, 1903, 329, 225.

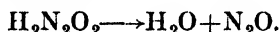
<sup>14</sup> Jones and Scott, *J. Amer. Chem. Soc.*, 1924, 46, 1545; Weitz and Vollmer, *Ber.*, 1924, 57B, 1015.

**Preparation and Properties of the Free Acid.**—Solutions of the acid are obtained when the silver salt is treated with hydrochloric acid, nitric acid, hydrogen sulphide, or phosphoric acid. A large excess of the silver salt is rubbed in a mortar with dilute cold HCl and filtered quickly.<sup>1</sup>

Silver hyponitrite is added in portions to an ethereal solution of hydrochloric acid until there is no more free hydrochloric acid. The filtered solution when evaporated in a desiccator leaves the free acid in the form of white leaflets, which easily explode when rubbed, especially in the presence of acid vapour or solid potassium hydroxide. The free acid is very soluble in water, and also dissolves in alcohol, ether, chloroform, and in benzene, but not in petroleum ether.<sup>2, 3</sup>

The molar weight, determined by the cryoscopic method in aqueous solution, is 59 ( $\text{H}_2\text{N}_2\text{O}_2$  requires 62).<sup>4</sup>

The acid does not expel  $\text{CO}_2$  from carbonates. When titrated it behaves much like carbonic acid, one-half of the hydrogen being neutralised at the phenolphthalein end point. In fact, as an acid it appears to be about as strong as carbonic acid (see Conductivity below). On standing it slowly changes into nitrous and nitric acids, and when an aqueous solution is boiled it gives  $\text{N}_2\text{O}$ . This hydrolysis is rapidly effected by sulphuric acid; nitrous oxide is the anhydride. The reaction is, however, not reversible :



In the presence of nitric acid hyponitrous acid can be boiled without decomposition. When freshly prepared, it should give only a faint yellow colour with potassium iodide; this effect is probably due to the nitrous acid formed by its decomposition. It is very stable towards reducing agents, although sodium bisulphite, followed by zinc and acetic acid, gives hydrazine.<sup>5</sup>

It is easily oxidised; potassium permanganate in acid solution converts it into nitric acid, in alkaline solution into a nitrite. Hyponitrites can be quantitatively titrated with permanganate.<sup>6</sup>

The heat of formation is negative, and has been determined by oxidising the calcium salt :<sup>7</sup>



The conductivity of the free acid is low, approximating to that of carbon dioxide; that of the salts is high on account of considerable dissociation and some hydrolysis.<sup>4</sup>

The following values of the equivalent conductivities refer to  $0^\circ \text{C.}$  :<sup>1</sup>

#### *Hyponitrous Acid.*

V=6.22	12.11	12.44	22.37	24.22	44.74	73.47	89.48	146.94
$\lambda=1.08$	1.49	1.52	2.12	2.39	3.10	3.85	4.21	5.43

<sup>1</sup> Rây, De, and Dhar, *J. Chem. Soc.*, 1913, 103, ii, 1562.

<sup>2</sup> Hantzsch and Kaufmann, *Annalen*, 1896, 292, 317.

<sup>3</sup> Tanatar, *Ber.*, 1894, 27, 187.

<sup>4</sup> Hantzsch and Sauer, *Annalen*, 1892, 299, 89.

<sup>5</sup> v. Brackel, *Ber.*, 1900, 33, 2115.

<sup>6</sup> Thum, *Monatsh.*, 1893, 14, 294.

<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1889, [6], 18, 571.

For the sodium and calcium salts the following values have been obtained :—

$\text{Na}_2\text{N}_2\text{O}_2$	.	.	$V=1685\cdot32$	$\lambda=68\cdot32$
$\text{CaN}_2\text{O}_2$	.	.	$V=1200$	$\lambda=73\cdot12$

The maximum equivalent conductivity of the sodium salt is about 68.

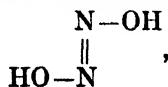
By introducing the Kohlrausch values for the conductivities of the sodium and calcium ion at  $0^\circ\text{C}$ ., and allowing for hydrolysis, the conductivity of the  $\text{NO}'$  ion is found to be 38·0 and 38·7 from the acid and its sodium salt.

**Structure.**—That this compound contains the diazo-group is indicated by many of the reactions used in its preparation, especially by the hydrolysis of organic compounds known to contain this group.

It is in fact a dioxime, as is shown more especially by its preparation from nitrous acid and hydroxylamine.

The molar weight is decided by the cryoscopic method, and the dibasic character of the acid by the neutralisation experiments and conductivities and by the existence of dialkyl derivatives and esters.

It has been suggested that hyponitrous acid is the antidioxime



the isomeric nitranide being perhaps the syn-compound.<sup>1</sup>

<sup>1</sup> Hantzsch, *Annalen*, 1898, 299, 67.

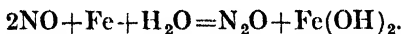


## CHAPTER X.

### THE OXIDES OF NITROGEN.

#### NITROUS OXIDE.

**History.**—Priestley<sup>1</sup> discovered nitrous oxide in 1772 when experimenting with the action of moist iron filings on nitric oxide (nitrous air):



He found that a gas remained which he termed “diminished nitrous air,” and that this gas behaved very much like ordinary air. Five years later Priestley<sup>2</sup> found that the same gas was obtained by the action of nitric acid on certain metals, especially tin and zinc.

Berthollet prepared the gas in 1785 by heating ammonium nitrate, but it was left to Davy<sup>3</sup> (1799) to make detailed investigations as to its properties. He showed that the combustions of a candle, phosphorus, sulphur, carbon, and iron wire were similar to those in oxygen. The gas was neutral to an extract of red cabbage, possessed a sweet taste and slight odour, and there was no diminution in volume when it was mixed with oxygen or nitric oxide. Davy discovered that inhalation produced an exhilaration, and he foresaw its use as an anæsthetic, notably in dentistry.<sup>4</sup>

The name “nitrous oxide” was first given by Davy, who also analysed the gas by burning carbon in a measured volume. Priestley and Lavoisier performed the volumetric analysis in a more accurate manner, and showed that nitrous oxide contained its own volume of nitrogen with one-half its volume of oxygen.

**Preparation.**—The gas may be prepared by the following methods:—  
1. Decomposition of ammonium nitrate by heat:



This method<sup>5</sup> is a common process for generating nitrous oxide, but the mixture becomes explosive unless the salt is free from organic impurities. It is advisable to melt the nitrate first to remove external moisture, and the decomposition begins at 170° C. Purification from nitric oxide and chlorine (from ammonium chloride) is effected by washing with ferrous sulphate and caustic soda solutions respectively. A modification<sup>6</sup> is to mix the ammonium nitrate with sand, pass the gas through ferrous sulphate or sodium sulphide solutions, and finally dry by washing with an emulsion of ferrous sulphate in concentrated sulphuric acid.

<sup>1</sup> Priestley, *Experiments on Air*, 1774, I, 118, 119; *ibid.*, 1775, II, 177.

<sup>2</sup> Priestley, *ibid.*, 1777, III, 133, 134, 139.

<sup>3</sup> Davy, *Works*, III, 54.

<sup>4</sup> Davy, *ibid.*, 276.

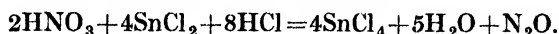
<sup>5</sup> Soubeiran, *J. Pharm. Chim.*, 1826, 13, 332.

<sup>6</sup> Lidoff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 59.

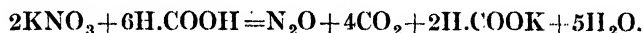
2. Another method <sup>1</sup> is by decomposing an equimolecular mixture of ammonium sulphate and sodium nitrate at 240° C., when a quiet, regular stream of nitrous oxide is evolved.

A number of methods have been described for the preparation of nitrous oxide by reduction of nitric acid or nitrates.

3. Nitric acid is reduced by means of stannous chloride.<sup>2</sup> A solution is made of 5 parts of stannous chloride, 10 parts of hydrochloric acid (sp. gr. 1.21), and 0.9 part nitric acid (sp. gr. 1.38), which on heating to boiling gives a regular stream of nitrous oxide :

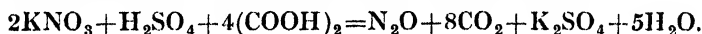


4. Another method <sup>3</sup> consists in the reduction of a nitrate by heating with anhydrous formic acid :



The reaction is started by heating, but once the gas begins to come off the source of heat is removed ; the gas is collected over a solution of caustic potash (20 per cent.) at 40° C., whereby the carbon dioxide is absorbed.

5. Oxalic acid <sup>4</sup> may also be used as a reducing agent. A solution of potassium nitrate, to which sulphuric acid has been added until the solution contains 20 per cent., is heated with oxalic acid :



6. Nitrous acid when reduced with hydrazine yields a mixture of nitrous oxide and ammonia : <sup>5</sup>



Hydroxylamine may also be used as a reducing agent.<sup>6</sup>

7. Sodium nitrite solution is treated with cooled concentrated hydroxylamine-hydrochloride solution, when the nitrous acid liberated by the hydrochloride is reduced by the hydroxylamine :



8. It is also possible to isolate nitrous oxide produced directly by the union of its elements in the nitrogen-oxygen flame. Spectroscopic examination will determine that in a certain part of the flame nitrous oxide is the chief product, and rapid cooling at this point will give a 25 per cent. yield of the gas.<sup>7</sup>

**Physical Properties.**—Nitrous oxide is a colourless gas with a pleasant odour and sweetish taste. When inhaled in small amounts it

<sup>1</sup> Thilo, *Chem. Zeit.*, 1894, 18, 532. See also W. Smith, *J. Soc. Chem. Ind.*, 1892, 11, 867; 1893, 12, 10.

<sup>2</sup> Compari, *Chem. Zentr.*, 1888, 1569. See also Gay-Lussac, *Ann. Chim.*, 1847, (iii), 23, 229.

<sup>3</sup> Quataroli, *Gazzetta*, 1911, 41, ii, 53.

<sup>4</sup> Desboursaux, *Compt. rend.*, 1903, 136, 1668.

<sup>5</sup> Francke, *Ber.*, 1905, 38, 4102.

<sup>6</sup> Pollak, *Annalen*, 1875, 175, 141.

<sup>7</sup> Pietet and Södermann, *French Patents*, 411785, 415594 (1910).

produces a feeling of exhilaration, while in larger quantities anæsthesia results, whence its extended application in minor operations, as in dentistry.

Its litre density at N.T.P., as determined by different investigators, is given as 1.9780,<sup>1</sup> 1.9777,<sup>2</sup> and 1.9774<sup>3</sup> grams. Compared with air as unity the density is 1.5301<sup>1</sup> and 1.5297.<sup>2</sup>

Nitrous oxide is easily liquefied,<sup>4</sup> and thus would be expected to show considerable deviation from Boyle's Law. The variation of volume with pressure has been studied by Rayleigh<sup>5</sup> at low pressures :

Pressure Ratio.	Volume Ratio.
75 mm. : 150 mm.	2.100066 : 1
$\frac{1}{2}$ atm. : 1 atm.	2.100827 : 1
1 atm. : 2 atm.	2.100651 : 1

The coefficient of expansion of nitrous oxide is 0.0037067.<sup>6</sup> The thermal conductivity at 0° C. has been given as 0.0000350,<sup>7</sup> 0.00003515,<sup>8</sup> and 0.00003530.<sup>9</sup> The value at 10° C. is 0.00003723,<sup>10</sup> and at 100° C. is 0.0000506.<sup>10</sup> The ratio of the specific heat at constant pressure to that at constant volume at 15° C. is 1.300 according to Partington and Shilling,<sup>11</sup> who have calculated this value from all reliable work. The value at 0° C. is 1.31, and at 100° C. 1.27.<sup>12</sup> The change of molar heat with temperature has been determined from 0° to 1000° C. :

$$C_p = 6.629 + 0.00694t - 0.0_5241t^2 ;$$

$$C_p = 8.659 + 0.00677t - 0.0_5222t^2 .^{13}$$

The viscosity of nitrous oxide is less than that of air according to the following table,<sup>14</sup> which shows the values of the coefficient of viscosity,  $\eta$ , in absolute (C.G.S.) units :—

$\eta \times 10^7$ .	Temperature, ° C.
1866	0
1441	15
1845	100

The refractive index of nitrous oxide for sodium light is 1.0000516.<sup>15</sup>

**Solubility.**—The following table gives the absorption coefficient,  $\beta$ , of nitrous oxide in water (see under Nitrogen, Solubility, p. 35) :—

- 
- <sup>1</sup> Leduc, *Compt. rend.*, 1905, 140, 642.  
<sup>2</sup> Rayleigh, *Proc. Roy. Soc.*, 1905, 74, 181.  
<sup>3</sup> Guye and Pintza, *Compt. rend.*, 1905, 141, 51.  
<sup>4</sup> Faraday, *Phil. Trans.*, 1823, p. 189.  
<sup>5</sup> Rayleigh, *loc. cit.*  
<sup>6</sup> Jolly, *Pogg. Annalen*, Jubelband, 1874, 151, 82.  
<sup>7</sup> Winkelmann, *ibid.*, 1875, 156, 497.  
<sup>8</sup> Eucken, *Physikal. Zeitsch.*, 1913, 14, 324.  
<sup>9</sup> Weber, *Ann. Physik*, 1917, 54, 437.  
<sup>10</sup> Stefan, *Chem. Zentr.*, 1875, 179.  
<sup>11</sup> Partington and Shilling, *The Specific Heats of Gases* (Benn, 1924).  
<sup>12</sup> Wullner, *Wied. Annalen*, 1878, 4, 321.  
<sup>13</sup> Shilling, *Phil. Mag.*, 1927, (vii), 3, 273.  
<sup>14</sup> C. J. Smith, *Proc. Phys. Soc.*, 1922, 34, 162.  
<sup>15</sup> Mascart, *Compt. rend.*, 1874, 78, 617. See also C. and M. Cuthbertson, *Phil. Trans.*, 1913, 213 [A], 1.

## SOLUBILITY OF NITROUS OXIDE IN WATER.

Temperature, ° C.	Bunsen, 1897. <sup>1</sup>	Roth, 1897. <sup>2</sup>	Geffcken, 1904. <sup>3</sup>
0	..	1.305	
5	1.0954	1.1403	1.048
10	0.9196	0.9479	0.8780
15	0.7778	0.7896	0.7379
20	0.6700	0.6654	0.6295
25	0.5961	0.5752	0.5444

In its solubility relations nitrous oxide obeys Henry's Law.<sup>4</sup> The gas is much more soluble in ethyl alcohol, as is seen by the results of Knopp:<sup>5</sup>

t° C.	0	5	10	15	20	25
$\beta^6$	4.178	3.844	3.541	3.268	3.025	2.853

The solubilities of nitrous oxide in aqueous salt solutions,<sup>3</sup> and also in solutions of aqueous glycerol,<sup>7</sup> are lower than those in water.

**Liquid Nitrous Oxide.**—Faraday<sup>8</sup> liquefied the gas at 0° C. under a pressure of 30 atmospheres. The liquid is colourless, mobile, and has a very faint odour of burnt sugar.

The refractive index is very low, the values for the sodium D line being 1.193 at 0° C.<sup>9</sup> and 1.3305 at 90° C.<sup>10</sup>

The critical data are given in the following table:—

## CRITICAL CONSTANTS OF NITROUS OXIDE.

Critical Temperature, ° C.	Critical Pressure, Atm.	Relative Critical Volume. <sup>11</sup>	Critical Density, Gram/c.c.	Authority.
35.4	75	..	..	Dewar, <i>Phil. Mag.</i> , 1884, (v), 18, 210.
36.4	73.07	0.0048	0.41	Cailletet and Mathias, <i>J. Physique</i> , 1886, [2], 5, 549.
38.8	77.5	0.00436	0.454	Villard, <i>Compt. rend.</i> , 1894, 118, 1096.
36.5	71.66	..	..	Cardoso and Arni, <i>J. Chim. phys.</i> , 1912, 10, 504.

<sup>1</sup> Bunsen, *Gasometrisches Methoden*, Braunschweig, 1877.

<sup>2</sup> Roth, *Zeitsch. physikal. Chem.*, 1897, 24, 114.

<sup>3</sup> Geffcken, *ibid.*, 1904, 49, 257.

<sup>4</sup> Findlay and Howell, *Trans. Chem. Soc.*, 1914, 291.

<sup>5</sup> Knopp, *Zeitsch. physikal. Chem.*, 1904, 48, 106.

<sup>6</sup>  $\beta$  is defined above under "Nitrogen, the Element." See p. 35.

<sup>7</sup> Henkel, *Dissertation*, Berlin, 1905.

<sup>8</sup> Faraday, *Phil. Trans.*, 1823, p. 189.

<sup>9</sup> Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339.

<sup>10</sup> Liveing and Dewar, *Phil. Trans.*, 1892, 34, 205.

<sup>11</sup> Defined as the ratio of the volume at  $t_c$  and  $p_c$  to that occupied by the same mass of gas at N.T.P.

The boiling-point of liquid nitrous oxide under 760 mm. pressure is given as  $-88.7^{\circ}\text{C}.$ <sup>1</sup>  $-87.9^{\circ}\text{C}.$ <sup>2</sup>

The variation of the boiling-point with the pressure is given in the following table :—

**VARIATION OF THE BOILING-POINT OF NITROUS OXIDE WITH THE PRESSURE.**

Pressure.	Boiling-point, °C.	Authority.	Pressure.	Boiling-point, °C.	Authority.
200 mm.	-90.1	{ Burrell and Robert-son, <i>loc. cit.</i>	13.19 atm.	-34	{ Cailletet and Mathias, <i>Compt. rend.</i> , 1886, 102, 1202.
730 „	-89.3		30.75 „	0	
760 „	-88.7		41.20 „	12	
4.6 atm.	-62	{ Cailletet and Mathias, <i>Compt. rend.</i> , 1886, 102, 1202.	45.30 „	16	
11.02 „	-40		49.40 „	20	

**DENSITIES OF LIQUID NITROUS OXIDE AT VARIOUS TEMPERATURES.**

Temperature, °C.	Density.	Authority.
-20.6	1.003	{ Cailletet and Mathias, <i>Compt. rend.</i> , 1886, 102, 1202.
- 7.3	0.953	
- 2.2	0.912	
0	0.9105	
10	0.856	{ Villard, <i>Compt. rend.</i> , 1894, 118, 1096.
17.5	0.804	
32.9	0.640	
36.3	0.572	

**Surface Tension.**—The surface tension at  $-89.3^{\circ}\text{C}.$  is 26.323 dynes per cm. The molar weight of the liquid, calculated at the critical temperature of  $36^{\circ}\text{C}.$ , is 43.52.<sup>3</sup>

The calculated molecular weights of both liquid and gaseous nitrous oxide from the critical data are 43.26 and 43.78, which shows that nitrous oxide is monomolecular in both states.<sup>4</sup>

**Heat of Formation.**—The molecular heat of formation of gaseous nitrous oxide is  $-17.740$  Cals.,<sup>5</sup> this value being the mean of the values obtained by the combustion of hydrogen in nitrous oxide and carbon monoxide in nitrous oxide. Berthelot's<sup>6</sup> value is  $-20.600$  Cals. The heat of formation of liquid nitrous oxide is given as  $-18.000$  Cals.<sup>6</sup>

<sup>1</sup> Liveing and Dewar, *Phil. Trans.*, 1892, 34, 205.

<sup>2</sup> Regnault, *Jahresber.*, 1863, p. 70.

<sup>3</sup> Grunmach, *Ann. Physik*, 1904, 15, 401.

<sup>4</sup> Grunmach, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, p. 1198.

<sup>5</sup> Thomsen, *Thermochemische Untersuchungen*, 1883, 2, 194.

<sup>6</sup> Berthelot, *Ann. Chim. Phys.*, 1880, [5], 20, 260.

The molecular heats of volatilisation at  $-20^{\circ}\text{C}$ .,  $0^{\circ}\text{C}$ ., and  $35^{\circ}\text{C}$ . are given as 2900, 2600, and 400 Cals. respectively.<sup>1</sup>

Evaporation *in vacuo* of a mixture of liquid nitrous oxide and carbon bisulphide causes the temperature to fall to  $-140^{\circ}\text{C}$ .

**Solid Nitrous Oxide.**—A snow-like mass is obtained by allowing liquid nitrous oxide to evaporate rapidly under reduced pressure.<sup>2</sup> Solid nitrous oxide melts at  $-102.3^{\circ}\text{C}$ .<sup>3</sup> The relationship between melting-point and vapour pressure is shown in the following table:—<sup>4</sup>

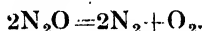
### VARIATION OF THE MELTING-POINT OF NITROUS OXIDE WITH THE PRESSURE.

Pressure, mm.	Melting-point, $^{\circ}\text{C}$ .	Pressure, mm.	Melting-point, $^{\circ}\text{C}$ .
650	— 91	100	—110.8
600	— 91.9	50	—117.2
500	— 93.9	30	—121.1
400	— 96.4	15	—127.0
300	— 99.5	7	—131.3
200	—103.7	4	—138.9
150	—106.7	1	—144.1

The equation of the curve is given by the expression :

$$\log P = -1096.72/t + 1.75 \log t + 0.0005t + 4.8665.$$

**Decomposition of Nitrous Oxide by Heat.**—This is one of the few examples of a gas reaction which takes place in the gas phase, at any rate in a silica vessel, as is shown by the fact that increase of surface (by the addition of powdered silica) has no effect on the velocity constant.<sup>5</sup> Since this latter is inversely proportional to the concentration the reaction is bimolecular; thus <sup>6</sup>



Initial $p$ (mm.)	296	139	52.5
Half-life (secs.)	255	470	860

The velocity constant is found to diminish with rise of temperature :

$T = 1125$	1085	1053	1030	1001	967	838
$\log_{10}(k \times 10^3) = 4.064$	3.575	3.223	2.940	2.580	2.133	0.040

From these results the "heat of activation" of nitrous oxide molecules is calculated from the Arrhenius equation

$$\frac{d \log k}{dt} = \frac{A}{RT^2},$$

$$\log k_2 - \log k_1 = \frac{A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

The mean value of  $A$  is 58.500 Cals. per mol.

<sup>1</sup> Caillietet and Mathias, *Ann. Chim.*, 1890, (vi), 21, 69.

<sup>2</sup> Wills, *Trans. Chem. Soc.*, 1874, 27, 21.

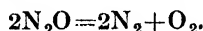
<sup>3</sup> Ramsay and Shields, *Chem. News*, 1893, 67, 190.

<sup>4</sup> Burrell and Robertson, *J. Amer. Chem. Soc.*, 1915, 37, 2641.

<sup>5</sup> Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, [A], 106, 284.

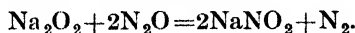
<sup>6</sup> Hunter, *Zeitsch. physikal. Chem.*, 1905, 53, 441. The photochemical decomposition has been studied by Macdonald, *J. Chem. Soc.*, 1928, p. 1.

**Chemical Properties of Nitrous Oxide.**—The outstanding chemical property of nitrous oxide is its ability to support vigorously the combustion of many substances. This is because of its ready decomposition into its elements, which begins at  $500^{\circ}\text{C}.$  and is complete at  $900^{\circ}\text{C}.$ , and all combustions in this gas are combustions in oxygen :



It will be seen that, after decomposition, the mixed gases contain one-third their volume of oxygen as compared with one-fifth in air.

A glowing splint is rekindled, and a taper burns brilliantly in the gas. Brightly burning sulphur, phosphorus, and carbon burn similarly as they do in oxygen. Sulphur which is only just burning is extinguished in the gas, as the temperature is not sufficient to cause decomposition. Sodium, potassium, and some other metals burn in nitrous oxide to produce in the first place peroxides, which when further heated yield nitrites and nitrates :



At lower temperatures nitrous oxide is a less vigorous oxidising agent than oxygen. Thus below  $350^{\circ}\text{C}.$  copper only forms cuprous oxide,  $\text{Cu}_2\text{O}$ , while potassium gives an oxide,  $\text{K}_2\text{O}_3$ , which absorbs further oxygen on being brought into the air.<sup>1</sup> Nitrous oxide, in common with the other oxides of nitrogen, is completely and quantitatively decomposed by passing the gas over red-hot copper.

Hydrogen reduces nitrous oxide in the presence of platinum black, finely divided palladium, or reduced nickel.

An unstable crystalline hydrate,  $\text{N}_2\text{O} + 6\text{H}_2\text{O}$ , is formed between nitrous oxide and water at a low temperature. Although by its formula nitrous oxide is the anhydride of hyponitrous acid,  $\text{H}_2\text{N}_2\text{O}_2$ , it will not combine with water to form this acid.

The most important use of nitrous oxide is as an anæsthetic. When mixed with oxygen and inhaled in small doses it produces a temporary exhilarating effect—hence the name “laughing gas.” Larger quantities of the mixed gases produce temporary unconsciousness, which generally lasts for about forty seconds. The amount of oxygen varies from 5 to 25 per cent., as the use of nitrous oxide alone involves danger of asphyxia.

It is important that the gas should be free from chlorine, nitric oxide, etc., when used for purposes of anæsthesia.<sup>2</sup>

**Detection and Estimation.**—Nitrous oxide may be distinguished from oxygen by its much greater solubility in water, its faint odour, and the fact that it does not react when brought into contact with nitric oxide.

Its ready reduction by hydrogen into nitrogen and water in the presence of finely divided metals may be used for its estimation, or it may be exploded with hydrogen in a Hempel apparatus.<sup>3</sup> Volumetrically, decomposition by an electrically heated iron wire which leaves a residual volume of nitrogen may be used. Gravimetrically, nitrous oxide may be decomposed by passing over red-hot copper and weighing the oxygen removed.

<sup>1</sup> Holt and Sims, *Trans. Chem. Soc.*, 1894, 65, 428.

<sup>2</sup> For purification and analysis of commercial samples, see Baskerville and Stephenson, *J. Ind. Eng. Chem.*, 1911, 3, 579.

<sup>3</sup> Hempel and Heymann, *Zeitsch. Elektrochem.*, 1906, 12, 600.

## NITRIC OXIDE.

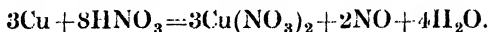
**History.**—Mayow in 1674 seems to have first prepared nitric oxide by the action of nitric acid on metals, such as iron, but it was Priestley<sup>1</sup> who, in 1772, first isolated and described the gas. He found that many metals with nitric acid produced a colourless gas which was only slightly soluble in water and produced no change with lime-water. The name of nitrous air was given to this gas by Priestley; it extinguished a taper, was noxious to animals, and was very soluble in a solution of green vitriol, which turned a dark colour. Priestley observed the formation of brown fumes when nitric oxide was mixed with air, and the fact that these fumes immediately dissolved in water.

The composition of nitric oxide was first investigated by Priestley<sup>2</sup> in 1786, who heated iron in nitric oxide by means of a burning glass. He noted an approximate diminution of one-half. Davy in 1800 carried out a similar experiment, but used carbon instead of iron, and, assuming that the carbon dioxide formed contained its own volume of oxygen, concluded that nitric oxide contained rather more than one-half its volume of oxygen and rather less than its volume of nitrogen.<sup>3</sup>

The exact volumetric composition of nitric oxide was demonstrated by Gay-Lussac<sup>4</sup> in 1809, who burnt metallic potassium in the gas and showed that the residual nitrogen occupied just one-half of the original volume. He rightly concluded that "this gas is composed of equal parts by volume of nitrogen and oxygen."

One of the most accurate determinations of the gravimetric composition of nitric oxide was carried out by decomposing a known weight of the gas with heated nickel. The nitrogen liberated was condensed on charcoal and weighed, while the oxygen content was found by determining the increase in the weight of the nickel.<sup>5</sup>

**Preparation.**—1. The action of nitric acid (sp. gr. 1.2) upon copper turnings or foil gives a ready stream of nitric oxide together with varying amounts of nitrous oxide and nitrogen. Ackworth<sup>6</sup> showed that accumulation of copper nitrate increased the amount of nitrous oxide, so that a purer gas is obtained by removing this solution at the bottom of a tower containing the copper:



Purification is best effected by washing the gas with water, absorbing in ferrous sulphate solution, and then expelling it from the latter solution by means of heat.

2. A purer form of nitric oxide is obtained by heating ferrous sulphate with nitric acid, or a mixture of ferrous sulphate and potassium nitrate with dilute sulphuric acid:



<sup>1</sup> Priestley, *Experiments on Air*, 1774, I, 109; 1777, III, Preface, p. 33; *Experiments and Observations*, 1779, IV, 48.

<sup>2</sup> Priestley, *Experiments and Observations*, 1786, VI, 304.

<sup>3</sup> Davy, *Works*, III, 77.

<sup>4</sup> Gay-Lussac, *Alémic Club Reprints*, IV, 14.

<sup>5</sup> Gray, *Trans. Chem. Soc.*, 1905, 87, 1601. See also under Atomic Weight, p. 59.

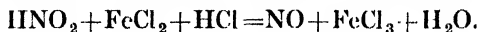
<sup>6</sup> Ackworth, *ibid.*, 1875, 28, 828.



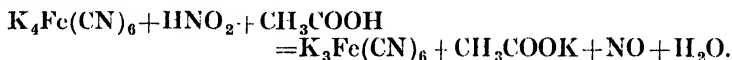
3. The action of potassium nitrate on a solution of ferrous chloride in hydrochloric acid also yields a fairly pure form of gas : <sup>1</sup>



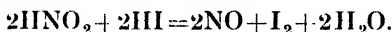
4. A convenient method of preparation is by dropping a concentrated solution of sodium nitrite into a solution of ferrous sulphate in sulphuric acid, or into a solution of ferrous chloride in hydrochloric acid : <sup>2</sup>



5. A slow stream of nitric oxide is obtained by dropping a solution of a mixture of potassium ferrocyanide and potassium nitrite into dilute acetic acid : <sup>3</sup>



6. A very pure form of gas may be prepared by dropping sulphuric acid (50 per cent.) on to a concentrated solution of potassium nitrite (2 parts) and potassium iodide (1 part) : <sup>4</sup>



7. Pure nitric oxide is formed in the Lunge nitrometer method of estimating nitrates, namely, by shaking nitric acid with excess of sulphuric acid and mercury. <sup>5</sup>

8. Nitric oxide is evolved when sulphur dioxide is passed through warm nitric acid (sp. gr. 1.15) : <sup>6</sup>



9. Electrolysis of a mixture of a 20 to 30 per cent. solution of nitric acid, containing 1 to 2 per cent. of nitrous acid, below 50° C. yields nitric oxide. <sup>7</sup>

10. Pure nitric oxide is produced when nitroso-diphenylamine is heated, either *in vacuo* (40° to 75° C.) or in air (180° to 190° C.). <sup>8</sup>

**Physical Properties.**—Nitric oxide is a colourless gas with a low boiling-point, heavier than air and sparingly soluble in water, giving (at first) a neutral solution. Its density relative to air has been determined as 1.0372 <sup>9</sup> and 1.0387. <sup>10</sup> The weight of 1 litre at N.T.P. is 1.3402 grams. <sup>11</sup>

Nitric oxide shows but little deviation from Boyle's Law. Jaquered and Scheuer <sup>12</sup> have determined the value of the coefficient  $\alpha_0$  in the equation

$$\alpha_0(p_1 - p_0) = 1 - \frac{p_1 v_1}{p_0 v_0}$$

between pressures of 400 mm. and 800 mm., and found it to be -0.00117.

<sup>1</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1847, (iii), 23, 203.

<sup>2</sup> Thiele, *Annalen*, 1889, 253, 246.

<sup>3</sup> Deventer, *Ber.*, 1893, 26, 589.

<sup>4</sup> Winkler, *ibid.*, 1901, 34, 1408.

<sup>5</sup> Emich, *Monatsh.*, 1892, 13, 73.

<sup>6</sup> Weber, *Pogg. Annalen*, 1867, 130, 277.

<sup>7</sup> Meister, Lucius, and Bruning, *German Patent*, 244362 (1912).

<sup>8</sup> Marquoyrol and Florentin, *Bull. Soc. chim.*, 1913, 13, 69.

<sup>9</sup> Dacomo and Meyer, *Annalen*, 1887, 240, 326.

<sup>10</sup> Leduc, *Compt. rend.*, 1893, 116, 322.

<sup>11</sup> Gray, *Proc. Chem. Soc.*, 1903, 56; Guye and Davila, *Compt. rend.*, 1905, 141, 826.

<sup>12</sup> Jaquered and Scheuer, *ibid.*, 1905, 140, 1384.

The coefficient of expansion between  $-140^{\circ}$  and  $0^{\circ}$  C. is 0.0037074.<sup>1</sup>

Regnault's value<sup>2</sup> for the specific heat at constant pressure ( $C_p$ ) is 0.23175, and the ratio  $C_p/C_v$  1.40. The value of  $C_p/C_v$ , according to Heuse,<sup>3</sup> is 1.38 at both  $15^{\circ}$  and  $-80^{\circ}$  C. It diminishes steadily at higher temperatures; thus:

Temperature, $^{\circ}$ C.	300	500	1000	1500	2000
$C_p/C_v$ .	1.399	1.393	1.375	1.347	1.317 <sup>4</sup>

The difference,  $C_p - C_v$  ( $=R$  for a perfect gas), also diminishes slightly at higher temperatures:

Temperature, $^{\circ}$ C.	300	500	1000
$C_p - C_v$ .	1.998	1.990	1.988 <sup>4</sup>

The variation of the molar heat at constant volume with the temperature is best expressed by the equation

$$C_v = 5.102 - 0.0564T + 0.009554T^2 - 0.0001934T^3.$$

Nitric oxide is an endothermic compound; the heat of formation is given as  $-21.575$  or  $-21.600$  Cals. at ordinary temperatures.<sup>5, 6</sup> That calculated for  $1841^{\circ}$  C. is  $-23.000$  Cals.<sup>4</sup>

The *viscosity*<sup>7</sup> of nitric oxide at  $0^{\circ}$  C. is  $1794 \times 10^{-7}$ .

The *refractive index* of nitric oxide for the sodium D line is 1.0002939.<sup>8, 9</sup>

The following table<sup>10</sup> gives the values of the absorption coefficient ( $\beta$ ) (see p. 35) of nitric oxide at various temperatures:—

#### SOLUBILITY OF NITRIC OXIDE IN WATER.

Temperature, $^{\circ}$ C.	Absorption Coefficient.	Temperature, $^{\circ}$ C.	Absorption Coefficient.
0	0.07381	40	0.03507
5	0.06461	50	0.03152
10	0.05709	60	0.02954
15	0.05147	70	0.02810
20	0.04706	80	0.02700
25	0.04323	90	0.02648
30	0.04004	100	0.02628

<sup>1</sup> Adventowski, *Bull. Acad. Sci. Cracow*, 1909, 742.

<sup>2</sup> Regnault, *Mém. de l'Acad.*, 1862, 26, 262.

<sup>3</sup> Heuse, *Ann. Physik*, 1919, [4], 59, 86.

<sup>4</sup> Shilling, *Trans. Faraday Soc.*, 1926, (vi), 22, 387, 388.

<sup>5</sup> Thomsen, *Thermochemische Untersuchungen*, 1906, p. 162.

<sup>6</sup> Berthelot, *Ann. Chim. Phys.*, 1880, [5], 20, 260.

<sup>7</sup> Vogel, *Ann. Physik*, 1914, (iv), 43, 1235; also Harrington, *Physical Review*, 1916, 8, 749.

<sup>8</sup> Cuthbertson and Metcalfe, *Proc. Roy. Soc.*, 1908, [A], 80, 406.

<sup>9</sup> C. and M. Cuthbertson, *Phil. Trans.*, 1913, 213 [A], 1.

<sup>10</sup> Winkler, *Ber.*, 1901, 34, 1408.

Nitric oxide is much more soluble in ethyl alcohol than in water, as is shown in the following table :—<sup>1</sup>

Temperature, ° C.	0	5	10	15	20	24
Absorption coefficient ( $\beta$ )	0.31606	0.29985	0.28609	0.27478	0.26592	0.26060

The formula expressing the value of the absorption coefficient between 0° and 24° C. is :

$$\beta = 0.31606 - 0.003487t + 0.000049t^2.$$

The solubility of nitric oxide in sulphuric acid has been determined by Tower.<sup>2</sup> The following table gives his results at 18° C. and 760 mm. in terms of the solubility coefficient ( $\beta'$ ) (see p. 35), which includes the vapour pressure of the solvent :—

### SOLUBILITY OF NITRIC OXIDE IN AQUEOUS SULPHURIC ACID.

Per cent. $\text{H}_2\text{SO}_4$ .	Sp. Gr. of Acid at 15° C.	Tension of Water Vapour.	Solubility Coefficient ( $\beta'$ ).
90	1.820	0.1 mm.	0.0193
80	1.733	0.4 „	0.0117
70	1.616	1.5 „	0.0113
60	1.503	3.1 „	0.0118
50	1.399	6.2 „	0.0120

The earlier work of Lunge<sup>3</sup> gave the values of 0.035 for 98 per cent.  $\text{H}_2\text{SO}_4$  and 0.017 for 60 per cent.  $\text{H}_2\text{SO}_4$ . Tower points out that for 98 per cent.  $\text{H}_2\text{SO}_4$  no constant results could be obtained owing to the solubility of the mercury in sulphuric acid in the presence of nitric oxide. Hence for quantitative work with the Lunge nitrometer concentrated acid should not be used. The most accurate results for the estimation of nitrates, nitrites, and oxides of nitrogen are obtained by using sulphuric acid of 70 per cent. concentration, in which both nitric oxide and air show a minimum solubility.

The absorption of nitric oxide by aqueous solutions of various salts has been the subject of much investigation. In the case of ferrous salt solutions the solubility of the gas increases with the concentration of the solution. The limit is reached when the proportions of iron to nitric oxide are in the ratio 1 : 1, both in aqueous and alcoholic solutions.<sup>4</sup> It is assumed that unstable chemical compounds are formed of the type  $\text{FeSO}_4\cdot\text{NO}$ ,  $\text{FeCl}_2\cdot\text{NO}$ , etc., but the ready dissociation of such compounds under the influence of heat indicates only a feeble combination. Usher<sup>5</sup> has investigated the freezing-point of such solutions,

<sup>1</sup> Bunsen, *Gasometrische Methoden* (Braunschweig, 1877).

<sup>2</sup> Tower, *Zeitsch. anorg. Chem.*, 1906, 50, 382.

<sup>3</sup> Lunge, *J. Soc. Chem. Ind.*, 1885, 4, 448; *Ber.*, 1885, 18, 1391.

<sup>4</sup> Manchot and Zechentmayer, *Annalen*, 1906, 350, 368. See also Kohlschutter, *Ber.*, 1907, 40, 877; Hüfner, *Zeitsch. physikal. Chem.*, 1907, 59, 416; also this series, Vol. IX., Part II.

<sup>5</sup> Usher, *Zeitsch. physikal. Chem.*, 1908, 62, 622.

and finds that neither the freezing-point nor the pressure of the nitric oxide remained constant, and hence no conclusion can be drawn as to the nature of the compound  $\text{FeSO}_4\cdot\text{NO}$ . The absorption of nitric oxide by bivalent salt solutions of nickel, cobalt, and manganese is of a similar nature.<sup>1</sup> Ferric salts also absorb nitric oxide readily,<sup>2</sup> as also do many metallic and non-metallic halides.<sup>3</sup> Nitric oxide dissolves in solutions of copper sulphate, producing a violet unstable compound,  $\text{CuSO}_4\cdot\text{NO}$ .<sup>4</sup> The solubility of the gas in cuprous halides in various solvents has been determined.<sup>5</sup>

According to Villard,<sup>6</sup> nitric oxide forms an unstable hydrate at  $0^\circ\text{C}$ . under a pressure of 10 atmospheres, or at  $12^\circ\text{C}$ . under 40 atmospheres, but not above  $12^\circ\text{C}$ . under any conditions.

From conductivity determinations of water through which nitric oxide is passed, Zimmermann<sup>7</sup> concludes that the gas is neither a weak nor a strong acid.

A purple solid is formed by nitric oxide and hydrogen chloride at  $-180^\circ\text{C}$ .<sup>8</sup> This melts at  $-150^\circ\text{C}$ . to a purple liquid, and is assumed to be an unstable complex of the type  $[\text{NOH}]^+\text{Cl}^-$ .

**Liquid Nitric Oxide.**—Faraday unsuccessfully attempted to liquefy nitric oxide at  $-110^\circ\text{C}$ . and under a pressure of 50 atmospheres, but the liquefaction was accomplished by Cailletet,<sup>9</sup> who allowed the gas to expand from a pressure of 104 atmospheres at  $-11^\circ\text{C}$ . Liquid nitric oxide is colourless in thin layers but slightly blue when examined in thick layers, which colour is probably due to traces of nitrogen trioxide.<sup>10</sup> The critical constants are shown in the following table :—

#### CRITICAL CONSTANTS OF NITRIC OXIDE.

Critical Temperature, $^\circ\text{C}$ .	Critical Pressure, Atm.	Critical Volume.	Critical Density.	Authority.
-93.5	71.2	..	0.524	Olszewski, <i>Compt. rend.</i> , 1885, 100, 940.
-92.9	64.4	..	..	Adventowski, <i>Bull. Acad. Sci. Cracov</i> , 1909, 742.

The variation of the boiling-point of liquid nitric oxide with the pressure is shown in the following table :—

<sup>1</sup> Hüfner, *Zeitsch. physikal. Chem.*, 1907, 59, 416.

<sup>2</sup> Manchot, *ibid.*, 1910, 72, 179. See also this series, Vol. IX., Part II.

<sup>3</sup> Beason, *Compt. rend.*, 1889, 108, 1012.

<sup>4</sup> Manchot, *Annalen*, 1900, 375, 308.

<sup>5</sup> Kohlschutter, *loc. cit.*

<sup>6</sup> Villard, *Compt. rend.*, 1888, 106, 1602.

<sup>7</sup> Zimmermann, *Monatsh.*, 1905, 26, 1277.

<sup>8</sup> Rodebush and Yutema, *J. Amer. Chem. Soc.*, 1923, 45, 332.

<sup>9</sup> Cailletet, *Compt. rend.*, 1877, 85, 1616.

<sup>10</sup> Travers, *Experimental Study of Gases* (Macmillan, 1901), p. 244.

### VARIATION OF THE BOILING-POINT OF NITRIC OXIDE WITH THE PRESSURE.<sup>1</sup>

Pressure.	Boiling-point, ° C.
356 mm.	—157·3
760 „	—150·2
9·8 atm.	—125·9
27·7 „	—109·2
55·6 „	— 96·3

Adventowski<sup>1</sup> assumes that liquid nitric oxide at low temperatures is polymerised on account of the anomalous vapour-pressure curve, and the high density at the boiling-point, 1·269, supports this view. It would appear, however, that complete dissociation has occurred at atmospheric pressure on account of the normal vapour density at this pressure.

The mean coefficient of expansion of liquid nitric oxide<sup>1</sup> between  $-140^{\circ}$  and  $0^{\circ}$  C. at 760 mm. is 0·0037074. The refractive index for sodium light,  $n_D$ , is 1·330.<sup>2</sup>

**Solid Nitric Oxide.**—Olszewski<sup>3</sup> obtained a snow-like mass by cooling liquid nitric oxide to  $-167^{\circ}$  C. under a pressure of 138 mm. According to Adventowski,<sup>1</sup> the melting-point of the solid is  $-160\cdot6^{\circ}$  C. at 168 mm. Liquid oxygen and solid nitric oxide combine explosively unless thoroughly cooled by complete immersion in liquid oxygen.<sup>4</sup>

**Chemical Properties.**—Nitric oxide is much more stable than nitrous oxide, and its decomposition by heat, which begins at  $500^{\circ}$  C. and is only slight at  $900^{\circ}$  C., is not complete until the very high temperature of  $1775^{\circ}$  C. is reached.<sup>5</sup> The formation of nitric oxide from its elements has been studied by Nernst,<sup>6</sup> and its decomposition by Jellinek.<sup>7</sup> A candle, burning sulphur, and feebly burning phosphorus are extinguished by the gas, because the temperatures are too low to bring about its decomposition. Brightly burning phosphorus, however, continues to burn with increased brilliancy, producing phosphoric oxide and leaving nitrogen. Burning carbon similarly removes the oxygen, while burning boron produces a mixture of boric acid and boron nitride.<sup>8</sup>

A number of metals are oxidised at a high temperature in nitric oxide, but if in a finely divided condition will reduce the gas at lower temperatures.<sup>9</sup>

Electric sparks passed through a mixture of sulphur vapour and

<sup>1</sup> Adventowski, *Bull. Acad. Sci. Cracow*, 1909, 742; *Zeitsch. f. Kompr. u. fluss. Gase*, 1910–11, 13, 19.

<sup>2</sup> Liveing and Dewar, *Phil. Mag.*, 1892, [5], 34, 205.

<sup>3</sup> Olszewski, *Compt. rend.*, 1885, 100, 940.

<sup>4</sup> Dewar, *Proc. Chem. Soc.*, 1895, 11, 225.

<sup>5</sup> Emich, *Monatsh.*, 1892, 13, 78, 615.

<sup>6</sup> Nernst, *Zeitsch. anorg. Chem.*, 1906, 49, 213.

<sup>7</sup> Jellinek, *ibid.*, 1906, 49, 229.

<sup>8</sup> Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [3], 52, 63; *Annalen*, 1858, 105, 69.

<sup>9</sup> Sabatier and Senderens, *Compt. rend.*, 1895, 120, 618, 1158.

nitric oxide give sulphurous and nitrous acids, which react further to give nitrosyl-sulphuric acid.<sup>1</sup>

Generally speaking, nitric oxide can be reduced in stages right down to ammonia. Thus, when the gas is mixed with hydrogen and brought into contact with platinum black, or finely divided nickel or copper,<sup>2</sup> tin, iron, or zinc,<sup>3</sup> ammonia is produced.

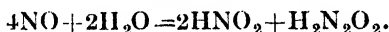
Stannous chloride reduces nitric oxide to hydroxylamine and ammonia, and also to hyponitrite if the solution is alkaline.

Chromous salts produce ammonia in neutral solution, and hydroxylamine if the solution is acid.<sup>4</sup>

Hydriodic acid reduces nitric oxide to ammonia.<sup>5</sup> Reduction to nitrous oxide is brought about by alkaline pyrogallol,<sup>6</sup> sulphurous acid,<sup>7</sup> phosphine (also some nitrogen),<sup>8</sup> and sulphuretted hydrogen and alkaline sulphides (with some ammonium sulphide).<sup>9</sup>

Many oxidising agents react with nitric oxide, producing chiefly nitric acid. Potassium permanganate, iodine, and hypochlorous acid yield nitric acid. Hydrogen peroxide gives nitrous and nitric acids. Silver oxide, manganese dioxide, lead dioxide, and red lead produce nitric acid. Chlorine peroxide gives nitrogen peroxide, while potassium chlorate and potassium iodate, heated in the gas, form nitrate and nitrogen peroxide with the liberation of halogens.<sup>10</sup>

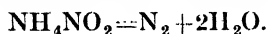
Nitric oxide reacts with water when preserved in contact for any length of time. According to Moser,<sup>11</sup> both dissolved oxygen and hydrions are responsible for the chemical changes which take place, producing, firstly, nitrous and hyponitrous acids: <sup>12</sup>



The hyponitrous acid breaks down, giving nitrous anhydride and also ammonia: <sup>13</sup>



This ammonia forms ammonium nitrite with the nitrous acid, and this breaks down with the liberation of nitrogen:



The amount of nitrogen increases with the length of time the nitric oxide is kept in contact with the water.

Potassium hydroxide in contact with nitric oxide for some months at the ordinary temperature produces a diminution of 75 per cent. in the volume. The residual gas is nitrous oxide, and potassium nitrite is found in the solution.<sup>14</sup> The reaction at 100° C. leaves a residue

<sup>1</sup> Chevrier, *Compt. rend.*, 1869, 69, 136.

<sup>2</sup> Sabatier and Senderens, *ibid.*, 1902, 135, 278.

<sup>3</sup> Faraday, *Pogg. Annalen*, 1834, 33, 149.

<sup>4</sup> Kohlschutter, *Ber.*, 1904, 37, 3053.

<sup>5</sup> Chapman, *Trans. Chem. Soc.*, 1867, 20, 169.

<sup>6</sup> Oppenheimer, *Ber.*, 1903, 36, 1744.

<sup>7</sup> Lunge, *ibid.*, 1881, 14, 2196.

<sup>8</sup> Dalton, *Ann. Phil.*, 1917, 9, 186; 10, 38, 83; *Gilbert's Annalen*, 1818, 58, 79.

<sup>9</sup> Lecomte, *Ann. Chim. Phys.*, 1847, [3], 21, 180.

<sup>10</sup> Auden and Fowler, *Chem. News*, 1895, 72, 163.

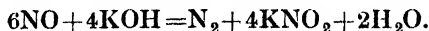
<sup>11</sup> Moser, *Zeitsch. anal. Chem.*, 1911, 50, 401.

<sup>12</sup> Zimmermann, *Monatsh.*, 1905, 26, 1277.

<sup>13</sup> Hantzsch and Kaufmann, *Annalen*, 1896, 292, 317.

<sup>14</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1848, [3], 23, 203.

which chiefly consists of nitrogen with a small amount of nitrous oxide.<sup>1</sup> At a higher temperature still, namely, 125° C., there is a diminution of 83.8 per cent., and the residual gas is entirely nitrogen : <sup>2</sup>

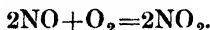


Nitric oxide combines with chlorine and bromine to form nitrosyl chloride, NOCl, and nitrosyl bromide, NOBr (with NOBr<sub>3</sub>), respectively, but with fluorine yields nitryl fluoride, NO<sub>2</sub>F :



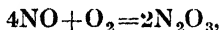
(See under Nitrogen and Halogens, p. 121.)

*The Oxidation of Nitric Oxide.*—The general explanation of the formation of ruddy fumes when nitric oxide is brought into contact with air or oxygen is that nitrogen peroxide is produced :



There seems to be little doubt that nitrogen peroxide is the final product, but it is by no means decided whether the above equation truly represents the mechanism of the oxidation.

In the first place, it would seem that nitrogen trioxide is the sole product when the oxidation is carried out below -110°, even with excess of oxygen :



and the production of nitrogen tetroxide only occurs above -100° : <sup>3</sup>

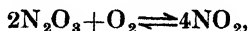


(See also p. 163.)

Raschig maintains that at ordinary temperatures a similar intermediate formation of the trioxide occurs, the second oxidation to the peroxide taking a much longer time.<sup>4</sup> According to Lunge,<sup>5</sup> however, the primary product of oxidation is the peroxide, the reaction being of the third order.

Further evidence in favour of nitrogen trioxide being the first oxidation product of nitric oxide, is the instantaneous formation of N<sub>2</sub>O<sub>3</sub> when nitric oxide and oxygen are mixed in the ratio of 4 to 1 at ordinary temperatures, the product remaining stable. When the proportions of nitric oxide and oxygen are as 2 : 1, the N<sub>2</sub>O<sub>3</sub> stage is reached very rapidly, then further oxidation to N<sub>2</sub>O<sub>4</sub> occurs, 34 per cent. in 20 seconds, and completely in 100 seconds.<sup>6</sup>

Sanfourche also maintains that the first stage in the oxidation of nitric oxide by dry air is nitrogen trioxide, which occurs instantaneously between -50° C. and 525° C. The second stage in the oxidation, which results in the formation of nitrogen peroxide, proceeds according to the equation



and is governed by the temperature.<sup>7</sup>

<sup>1</sup> Russell and Lepraik, *Trans. Chem. Soc.*, 1877, 31, 37.

<sup>2</sup> Emich, *Monatsh.*, 1892, 13, 90.

<sup>3</sup> Francesconi and Sciacca, *Gazzetta*, 1904, 34, i, 447.

<sup>4</sup> Raschig, *Zeitsch. angew. Chem.*, 1904, 17, 1777 ; 1905, 18, 121.

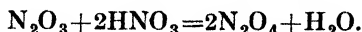
<sup>5</sup> Lunge, *ibid.*, 1906, 19, 807 ; 1907, 20, 1717.

<sup>6</sup> Jolibois and Sanfourche, *Compt. rend.*, 1919, 168, 235.

<sup>7</sup> Sanfourche, *ibid.*, 1919, 168, 307.

The first oxidation product, even in presence of water, is stated to be the trioxide and not the peroxide. The nitrogen trioxide is then decomposed by water to form nitric acid and nitric oxide.<sup>1</sup>

In the presence of nitric acid, Sanfourche considers that nitrogen trioxide is oxidised to form the peroxide and water :

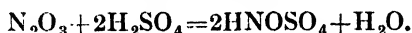


It cannot be said that the mechanism of the oxidation has been definitely settled. One of the chief difficulties encountered is the fact that nitrogen trioxide behaves chemically as if its formula were  $\text{N}_2\text{O}_3$ , whereas its physical properties indicate that it is an equimolecular mixture of nitric oxide and nitrogen tetroxide. Thus it is probable that Lunge's theory as to the primary formation of nitrogen peroxide is correct, as this oxide would then combine with unoxidised nitric oxide to form nitrogen trioxide :



It has been shown that under ordinary conditions nitrogen peroxide, nitric oxide, and nitrogen trioxide can exist in equilibrium,<sup>2</sup> which means that oxidation of nitric oxide in the presence of an absorbent results in the removal of nitrogen tetroxide, together with an equivalent of nitric oxide in the form of nitrogen trioxide.

The use of suitable absorbents is of fundamental importance in determining the products of oxidation of nitric oxide. In the case of concentrated sulphuric acid, both Raschig and Lunge agree that a mixture of nitric oxide and nitrogen peroxide is absorbed as nitrogen trioxide to produce nitrosyl-sulphuric acid :

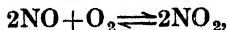


Nitrogen tetroxide is also absorbed by concentrated sulphuric acid, and a rise in temperature causes the reaction to move in the reverse direction :<sup>3</sup>



Aqueous alkalis do not completely absorb either nitrogen trioxide or nitrogen tetroxide, since secondary reactions occur which are due to the water present. These will be discussed in detail under the respective oxides.

The kinetics of the oxidation of nitric oxide can be dealt with in two ways, according as to whether the final product is  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$ . If it be assumed that the reaction is represented by



*i.e.* that the nitrogen tetroxide is completely dissociated, then the reaction velocity is expressed by the usual trimolecular equation

$$\frac{dx}{dt} = K(a-x)^2(c-x),$$

<sup>1</sup> Sanfourche, *Compt. rend.*, 1919, 168, 401. See also Schmidt and Bocker, *Ber.*, 1906, 39, 1368; Le Blanc, *Zeitsch. Elektrochem.*, 1906, 12, 541; Briner, Niewiaski, and Wiswald, *J. Chim. phys.*, 1922, 19, 290.

<sup>2</sup> Dixon and Peterkin, *Trans. Chem. Soc.*, 1899, 75, 629.

<sup>3</sup> Lunge and Weintraub, *Zeitsch. angew. Chem.*, 1899, 12, 417.



where

$2a$  = initial concentration of NO,  
 $c$  = " " " " O<sub>2</sub>,  
 $x$  = amount transformed in time  $t$ .

On integration the velocity constant is given by the equation

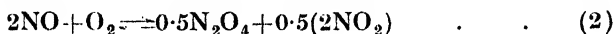
$$K = \frac{1}{t} \cdot \frac{1}{(c-a)^2} \left\{ \frac{(c-x)x}{a(a-x)} + \log_e \frac{c(a-x)}{a(c-x)} \right\}.$$

The value of  $K$  can be calculated from the experimental work of Lunge and Berl<sup>1</sup> on the oxidation of mixtures of nitric oxide and air.

The above expression ignores the change in volume in the system, although this error may be minimised by calculating  $K$  for successive small intervals of time. An expression is given by Wegscheider<sup>2</sup> to correct for this volume error both in the equation—



and also in the reaction which assumes that one-half of the N<sub>2</sub>O<sub>4</sub> is dissociated:



This expression is—

$$\frac{d\mu}{dt} = - \frac{K(M_1 - 2\mu)^2(M_2 - \mu)}{\left(V - \frac{RT}{P}b\mu\right)},$$

where  $M_1$  = initial concentration of NO,

$M_2$  = " " " " O<sub>2</sub>,

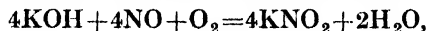
$\mu$  = volume of oxygen changed in time  $t$  in 100 volumes of mixture,

$V$  = total initial volume of gas at temperature  $T$  and pressure  $P$ , these two latter being constant under the conditions of the experiment,

$b$  = 1 in equation (1) and 1.5 in equation (2).

Further work on the oxidation of nitric oxide has been carried out by Bodenstein;<sup>3</sup> he investigated the variation of the velocity constant with temperature; Todd<sup>4</sup> investigated this from the standpoint of constant volume and constant pressure reactions.

**Detection and Estimation.**—Nitric oxide can easily be detected by the formation of brown fumes when brought into contact with air or oxygen. This oxidation can also be utilised as a means of estimation by absorbing the nitrogen trioxide by dry potassium hydroxide,



as four-fifths of the total contraction observed by the addition of a known volume of air or oxygen is nitric oxide.<sup>5</sup> Monoethyl aniline<sup>6</sup> may be used instead of caustic potash with advantage, as it does not absorb N<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, or CO. Another method of estimation<sup>7</sup> is to

<sup>1</sup> Lunge and Berl, *Zeitsch. angew. Chem.*, 1906, 19, 860.

<sup>2</sup> Wegscheider, *Zeitsch. physikal. Chem.*, 1900, 35, 577.

<sup>3</sup> Bodenstein, *Zeitsch. Elektrochem.*, 1918, 24, 183.

<sup>4</sup> Todd, *Phil. Mag.*, 1918, 35, 281.

<sup>5</sup> Klinger, *Ber.*, 1912, 45, 3231.

<sup>6</sup> Koehler and Marquayrol, *Bull. Soc. chim.*, 1913, 13, 69.

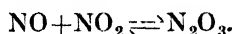
<sup>7</sup> Knorre, *Chem. Ind.*, 1902, 534.

observe the contraction which occurs when a gas containing nitric oxide is brought into contact with acidified potassium bichromate. In this case complete oxidation to nitric acid takes place.

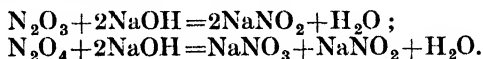
Potassium permanganate<sup>1</sup> will also bring about a similar oxidation, but in this case an acidified standard solution is used, and the amount of permanganate used up is determined by ordinary volumetric methods.

Reduction<sup>2</sup> of nitric oxide to nitrogen may be brought about by passing the gas mixed with hydrogen over heated platinum black.

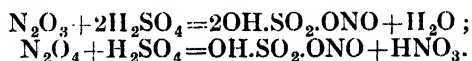
None of the foregoing methods are applicable if a mixture of gases containing nitric oxide, nitrogen trioxide, and nitrogen peroxide is to be analysed, owing to the interaction of nitric oxide and nitrogen peroxide :



An approximate estimation may be made by absorbing the gases in an aqueous solution of sodium hydroxide and determining the amounts of nitrite and nitrate present, formed by the following reactions :—



A mixture of gases which contains the nitric oxide in smaller amount than that required by the tetroxide to form  $\text{N}_2\text{O}_3$  may be analysed by absorption in concentrated sulphuric acid (85 to 95 per cent.) :



This nitrosyl-sulphuric acid can be estimated by means of potassium permanganate, and the total nitrogen by the nitrometer, and the relative proportions of the gases can thus be calculated.

When the nitric oxide is in excess of the amount required by the peroxide to form  $\text{N}_2\text{O}_3$ , a combination of two methods<sup>3</sup> may be used. The absorption is first effected in concentrated sulphuric acid, and the gases are then passed through an absorption tube containing acidified potassium permanganate.

**The Nitric Oxide Equilibrium and Synthesis.—Historical.**—Since the times of Priestley and Cavendish in the latter part of the eighteenth century, it has been known that the passing of electric sparks through air gives “nitric acid,” *i.e.* oxides of nitrogen absorbable by potash with the production of nitre. It was noticed by Crookes that the combination occurred in a high-tension arc.<sup>4</sup> He was awake to the necessity of securing a sufficient supply of combined nitrogen for agricultural purposes. The nitric oxide synthesis was from this time largely investigated with a view to technical use. Rayleigh passed sparks from an induction coil through an oxygen-nitrogen mixture containing 36 per cent. of the latter gas, in the presence of excess of alkali which was circulated continuously. The yield was at the rate of 56 grams  $\text{HNO}_3$  per kilowatt hour.<sup>5</sup> A number of arcs drawn out by rotation was used to increase the concentration of electrical energy, but it was found that this soon reached a useful limit, beyond which the

<sup>1</sup> Moser, *Zeitsch. anal. Chem.*, 1911, 50, 401.

<sup>2</sup> Knorre and Arendt, *Ber.*, 1899, 32, 2136.

<sup>3</sup> Webb, *Absorption of Nitrous Gases* (Arnold, 1923), p. 345.

<sup>4</sup> Crookes, *Chem. News*, 1892, 65, 302.

<sup>5</sup> Rayleigh, *Trans. Chem. Soc.*, 1897, 71, 181.

yield of NO no longer increased.<sup>1</sup> About the end of the century the equilibrium conditions began to be studied, and especially the degrees of combination which could be effected by heat alone.

Although some combination can be effected when the gases are passed over platinum black at 250° C.,<sup>2</sup> yet high temperatures are generally required for the synthesis. The oxides of nitrogen are formed in many combustions,<sup>3</sup> such as that of carbon in highly compressed air,<sup>4, 5</sup> or of hydrogen, or in the presence of a platinum wire raised to a white heat by an electric current. The combustion of hydrogen and nitrogen under lime-water seems to afford a possible method of "fixation."<sup>6</sup>

*The Thermal Equilibria.*—Nitric oxide is formed from its elements with absorption of 21·600 Cals. per mol. of NO. The gas is in a state of false equilibrium at the ordinary temperatures, although some observers had found a considerable stability towards heat.<sup>7</sup> When heated to between 500° and 1000° C., however, in a tube it begins to decompose, and the decomposition is considerable at 1200° C.<sup>8</sup> At high temperatures small equilibrium amounts of NO are formed from the elements.

The thermal equilibria in mixtures heated by arcs showed an increase in the amount of NO with diminution in the size of the arc, and therefore presumably at higher temperatures.<sup>9</sup>

On account of the endothermic character of the reaction



it shifts more to the right at the highest temperatures.

The equilibrium percentages of NO have been found experimentally : <sup>10</sup>

Temperature, ° abs.	=1811	1877
Per cent. of NO (x)	=0·37	0·42

From these a constant  $\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$  can be calculated, and from the reaction isochor,

$$\log K_2 - \log K_1 = \frac{q}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right),$$

the variation of the constant with temperature is determined. Over the range of temperatures given, the heat of reaction "q" does not vary much with the temperature :

T.° abs.	1500	1800	1811	2000	2033	2195	2500	2580	2675	2900	3200
x (found)			0·37		0·64	0·97		2·05	2·23		5
10 <sup>3</sup> K	2·48	8·51	9·16	15·3	15·9	24·2	45·5	52·1	56·8	82·9	117·9
x <sub>1</sub>	0·10	0·34	0·35	0·61	0·67	0·98	1·79	2·04	2·37	3·20	4·43

x<sub>1</sub> is calculated in the case of air by means of the equation—

<sup>1</sup> McDougall and Howles, *Mem. Manchester Phil. Soc.*, 1900, (iv), 44, No. 13.

<sup>2</sup> See Wöhler, *Ber.*, 1903, 36, 3479; Loew, *J. Agric. Sci.*, 1910, 3, 320; contrast Russell and Smith, *ibid.*, 1906, 1, 144.

<sup>3</sup> Spottiswoode, *Proc. Roy. Soc.*, 1881, 31, 173.

<sup>4</sup> Hempel, *Ber.*, 1890, 23, 1457.

<sup>5</sup> Berthelot, *Compt. rend.*, 1900, 130, 1345, 1430, 1662.

<sup>6</sup> Brunler, *Chemical Age*, 1926, 14, 29 (9th January).

<sup>7</sup> Berthelot, *Compt. rend.*, 1874, 77, 1448.

<sup>8</sup> Emich, *Monatsh.*, 1892, 13, 73, 615.

<sup>9</sup> Muthmann and Hofer, *Ber.*, 1904, 36, 438.

<sup>10</sup> Nernst and Jellinek, *Zeitsch. anorg. Chem.*, 1906, 49, 213; Finckh, *ibid.*, 1908, 45, 116.

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right)\left(20.8 - \frac{x}{2}\right)}$$

When these equilibria are obtained by heating the gases to the highest available temperatures, they must be "fixed" by rapid cooling. In this connection the velocities of the direct and inverse reactions are important.<sup>1</sup> The following values refer to air at atmospheric pressure :—

(a) Time required to half decompose the equilibrium amount of NO—

Temperature, ° abs. . . . .	900	1500	1900
Time in secs. . . . .	7350	3.8 mins.	1 sec.

(b) Time required to form half the theoretical amount of NO—

Temperature, ° abs. . . . .	1500	1900
Time in secs. . . . .	1810 mins.	2.08 mins.

The decomposition of nitric oxide at the surface of a heated platinum wire has been studied,<sup>2</sup> and the reaction  $2\text{NO} = \text{N}_2 + \text{O}_2$  found to be unimolecular with respect to nitric oxide. The reaction is retarded by oxygen but is not influenced by nitrogen.

*The Effects of Electrical Discharge.*—Although the silent discharge has long been known as a powerful agent in chemical synthesis, the spark or arc discharge had, until the last quarter of the nineteenth century, been regarded chiefly, if not solely, as a convenient means for localising a high temperature inside a closed vessel. The elucidation of the mechanism of conduction through gases has shown that the molecules are profoundly affected, and that this may lead to specific chemical effects, apart from those due to the temperatures of the spark, etc.

The conducting particles in a gas are free electrons and molecules or atoms which have been positively or negatively charged by the gain or loss of one or more electrons. These gaseous ions may combine, with mutual neutralisation of charges, thus accounting for such chemical effects as the synthesis of  $(\text{CN})_2$ , HCN, etc., by the silent discharge, of ozone perhaps by the union  $\text{O}_3^+$  and  $\text{O}^-$ , and of NO perhaps by the union of  $\text{N}^-$  and  $\text{O}^+$ . These compounds are formed in appreciable quantities at ordinary temperatures by the silent discharge, and correspond to electrical equilibria, which are different from the ordinary equilibria.<sup>3</sup>

When a gradually increasing voltage is applied to two electrodes separated by a gas or mixture of gases, a small current or non-luminous discharge passes at first which produces no chemical effects. It is due to the ions and electrons naturally present in the gas. At a certain voltage, which naturally varies with the material, dimensions, and separation of the electrodes, a glow or brush discharge is seen. This discharge is stable, for an increase of current necessitates an increased voltage, therefore at a given voltage the current reaches a maximum. This kind of discharge produces ions by collision between electrons and

<sup>1</sup> Nernst and Jellinek, *loc. cit.*

<sup>2</sup> Green and Hinshelwood, *Trans. Chem. Soc.*, 1926, 129, 1709.

<sup>3</sup> Warburg and Leithauser, *Drude's Annalen*, 1906, 20, 743; 1907, 23, 209; Berthelot, *Ann. Chim. Phys.*, 1906, [8], 8, 9, 145.

gas molecules, and hence initiates chemical changes. If the current "I" is increased still further, the voltage "E" falls, the conductivity rapidly increases, and the brush discharge is succeeded by the high-tension arc. In this the charged particles are produced in large quantities by impact, the resistance of the gap decreases more rapidly than the current increases, or an increase of current is accompanied by a decrease in the voltage. Such arcs are therefore electrically unstable. The temperature rises continuously and the resistance decreases until the arc passes, with a slight discontinuity in the "E, I" graph, into the ordinary low-tension or lighting arc, in which the current is mainly carried by electrons from the cathode and positively charged ions from the material of the anode. On this account, in spite of its high temperature, such an arc is useless for the synthesis of NO. It is necessary to maintain the high-tension arc by electrical devices. A resistance of the metallic kind (which obeys Ohm's Law) is placed in series with the direct current arc. An increase of current increases the voltage drop across this, and therefore decreases that available for the arc. In alternating current arcs the resistance is replaced by an inductance.

In such arcs an electrical equilibrium is set up between the nitrogen and oxygen which is not the same as the thermal equilibrium, and which only exists when and where the gases are under the influence of the discharge, or perhaps for a short distance beyond (or time after) the discharge. This kind of arc is probably due to the formation of atomic nitrogen and oxygen.<sup>1</sup>

In a high-tension arc at 2000° C., NO can be produced in amounts which would be in thermal equilibrium with N<sub>2</sub> and O<sub>2</sub> at 4500° to 5000° C. Allmand and Ellingham consider that the law of mass or concentration action does not apply to these electrical equilibria.<sup>2</sup>

The theory that the electrical discharge merely supplies a localised high temperature<sup>3, 4</sup> does not account for the facts.

It was shown on the experimental scale<sup>5</sup> that the gases sucked from the middle of a 3 cm. steady vertical arc through a water-cooled platinum capillary tube contain 5 per cent. of NO, corresponding to the thermal equilibrium at 3000° C.<sup>5</sup>

Haber and his co-workers also used a vertical arc between electrodes of platinum or iron.<sup>6, 7</sup> Using air, and with iron electrodes, they obtained nearly 10 per cent. of NO, and with a mixture of equal volumes of N<sub>2</sub> and O<sub>2</sub> passed at a slow rate (0.8 litre per hour), 14.4 per cent. of NO. The voltages employed were from 2050 to 4800, and the current from .205 to .306 amp. The temperatures corresponding to these yields in the purely thermal equilibrium were certainly not reached. As the arc was an alternating one and was extinguished at every half-period, there must have been great variations of temperature, which would still further reduce the mean value of this. A short direct current arc at 2700° C. with a cooled anode gave up to 9 per cent. of NO from

<sup>1</sup> Durand and Naville, *J. Chim. phys.*, 1908, 6, 137 1909, 7, 1; 1914, 12, 526; 1915, 13, 18; 1919, 17, 329.

<sup>2</sup> Allmand and Ellingham, *Applied Electrochemistry* (Arnold, 1924).

<sup>3</sup> Muthmann and Hofer, *Ber.*, 1904, 36, 438.

<sup>4</sup> Brode, *Zeitsch. Elektrochem.*, 1905, 11, 752.

<sup>5</sup> Grau and Russ, *ibid.*, 1907, 13, 345, 573.

<sup>6</sup> Haber and König, *ibid.*, 1907, 13, 725; 1908, 14, 689.

<sup>7</sup> Haber and Platow, *ibid.*, 1910, 16, 798.

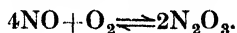
air. If all the air had been heated to this temperature (which can never occur), the maximum yield should have been not more than 4 per cent.<sup>1, 2</sup>

Oxides of nitrogen may also be obtained from the air by silent discharge at the ordinary temperatures,<sup>3, 4</sup> in which case the combination must take place through the ions produced by this discharge.

It has been further discovered that the conditions of maximum yield per hour in any given apparatus (space-time yield) do not correspond to a very slow passage through the high-tension arc (with maximum percentage conversion), but to a moderate speed. The presence of water-vapour diminishes the yield.<sup>5</sup>

### NITROGEN TRIOXIDE.

**Preparation.**—1. The mixing of nitric oxide and oxygen in any proportion below  $-110^{\circ}$  C. results in production of nitrogen trioxide :<sup>6</sup>

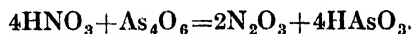


For example, when nitric oxide is passed through liquid oxygen at  $-185^{\circ}$  C. a green solid,  $(\text{N}_3\text{O}_4)_x$ , is first formed, which at a slightly higher temperature is converted into blue  $\text{N}_2\text{O}_3$ .

An impure form of the trioxide is produced as a bluish liquid when a mixture of nitric oxide and nitrogen peroxide is cooled to  $-30^{\circ}$  C. :



2. The reduction of nitric acid by arsenious oxide yields nitrogen trioxide :<sup>7</sup>



Lunge stated that nitric acid of specific gravity 1.35 gives pure nitrogen trioxide ; but Ramsay and Cundall<sup>8</sup> used acid of specific gravity 1.5 and carried out the preparation as follows : The mixture of acid and arsenious oxide is warmed on a water-bath until the reaction starts, when the source of heat is removed and, if necessary, the retort (or distilling flask) is cooled. The fumes are passed over fused calcium nitrate (or chloride) and phosphoric oxide and condensed in a U-tube immersed in a freezing mixture of ice and salt. The bluish-green liquid is then redistilled in an atmosphere of nitric oxide, passed over phosphoric oxide, and again liquefied at  $-10^{\circ}$  C., when the product is a deep blue liquid which, however, contains traces of nitrogen tetroxide.

3. By passing a spark discharge<sup>9</sup> through liquid air a flocculent green precipitate is obtained, which, after evaporation of the liquid air, leaves the trioxide as an amorphous blue powder, melting at  $-111^{\circ}$  C.

<sup>1</sup> Morden, *Trans. Amer. Electrochem. Soc.*, 1908, 14, 113.

<sup>2</sup> Holweh and König, *Zeitsch. Elektrochem.*, 1910, 16, 803.

<sup>3</sup> Warburg and Leithauser, *Drude's Annalen*, 1906, 20, 743 ; 1907, 23, 299.

<sup>4</sup> Berthelot, *Ann. Chim. Phys.*, 1906, [8], 8, 9, 145.

<sup>5</sup> Tartar and Perkins, *J. Physical Chem.*, 1926, 30, 595.

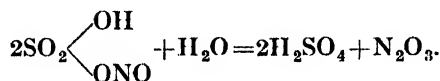
<sup>6</sup> Francesconi and Sciacca, *Gazzetta*, 1904, 34, (i), 447 ; Helbig, *Atti R. Accad. Lincei*, 1903, 5, 166 ; Raschig, *Chem. Zeit.*, 1911 35, 1096 ; Hasche, *J. Amer. Chem. Soc.*, 1925, 47, 2143.

<sup>7</sup> Lunge, *Ber.*, 1878, 11, 1229.

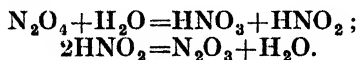
<sup>8</sup> Ramsay and Cundall, *Trans. Chem. Soc.*, 1885, 47, 187.

<sup>9</sup> Helbig, *Atti R. Accad. Lincei*, 1903, [V], 12, i, 166 ; Muller, *Zeitsch. anorg. Chem.*, 1912, 72, 330 ; Raschig, *ibid.*, 1913, 84, 115.

4. The action of water upon nitrosyl-sulphuric acid (chamber crystals) results in the formation of nitrogen trioxide: <sup>1</sup>



5. Nitrogen tetroxide yields the trioxide when decomposed by a small quantity of water:



6. Liquid nitrogen tetroxide, when saturated with nitric oxide, and subsequently cooled, yields dark blue crystals of nitrogen trioxide: <sup>2</sup>



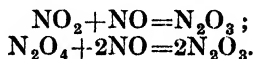
An impure form of the trioxide is produced as a bluish-green liquid when a mixture of gaseous nitrogen peroxide and nitric oxide is cooled to  $-30^\circ \text{C}$ .

7. Mineral acids decompose sodium nitrite with the liberation of nitrogen trioxide. Thus when a 20 per cent. solution of sodium nitrite is decomposed by concentrated sulphuric acid, a greenish colour is produced, and a gaseous mixture of nitrogen peroxide and nitric oxide in the proportions to form the trioxide is liberated:



8. The action of a diluted nitric acid (5N or 6N) upon copper gives nitrogen trioxide entirely as the gaseous product. <sup>3</sup>

**Physical Properties of Nitrogen Trioxide.**—Nitrogen trioxide under ordinary conditions is a brown gas which behaves as though it were a mixture of molecular proportions of nitrogen peroxide and nitric oxide. Much investigation has taken place as to the real existence of gaseous nitrogen trioxide. No marked contraction occurs when gaseous nitrogen peroxide and nitric oxide are mixed, as should happen if either of the following reactions took place:—<sup>4</sup>



A small diminution, however, does occur, which is consistent with the presence of 3 per cent. of undissociated nitrogen trioxide. <sup>5</sup>

The vapour density of gaseous nitrogen trioxide obtained from the liquid, which has been subjected to prolonged drying, indicates that the gas is made up of a mixture of  $\text{N}_4\text{O}_6$  and  $\text{N}_2\text{O}_3$  molecules. Traces of moisture dissociated the larger into the smaller molecules. <sup>6</sup>

The boiling-point of liquid nitrogen trioxide is approximately

<sup>1</sup> Rammelsberg, *Ber.*, 1872, 5, 310; Streiff, *ibid.*, 1872, 5, 285.

<sup>2</sup> Wittorf, *Zeitsch. anorg. Chem.*, 1904, 41, 85; Porschaew, *ibid.*, 1894, 7, 214; Péligot, *Ann. Chim. Phys.*, 1841, (iii), 2, 58.

<sup>3</sup> Bagster, *Trans. Chem. Soc.*, 1921, 119, 82.

<sup>4</sup> Ramsay and Cundall, *ibid.*, 1890, 57, 590.

<sup>5</sup> Dixon and Peterkin, *ibid.*, 1899, 75, 614.

<sup>6</sup> Baker, *ibid.*, 1907, 91, 1862.

$-2^{\circ}\text{C.}$ , although after prolonged drying the boiling-point may rise to  $48^{\circ}\text{C.}$ <sup>1</sup> Under ordinary pressures the liquid is stable up to  $-21^{\circ}\text{C.}$ <sup>2</sup> According to Baume and Roberts,<sup>3</sup> the boiling-point of pure  $\text{N}_2\text{O}_3$  is  $-27^{\circ}\text{C.}$  at 760 mm. The variation of the density of liquid nitrogen trioxide with the temperature is shown in the following table :—<sup>4</sup>

Temperature, $^{\circ}\text{C.}$ . . . . .	-8	-4	-1	0	1	2
Density . . . . .	1.4640	1.4555	1.4510	1.4490	1.4485	1.4470

The melting-point diagram of the system  $\text{N}_2\text{O}_3\text{--NO}_2$  is normal, and shows a single eutectic in the neighbourhood of pure  $\text{N}_2\text{O}_3$ .<sup>3</sup> (See under Nitrogen Tetroxide, p. 174.)

**Dissociation of Nitrogen Trioxide.**—The dissociation of nitrogen trioxide under various conditions of temperature and drying has been studied by Jones.<sup>5</sup> He concludes that three distinct reactions proceed :

- (a)  $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$  ;
- (b)  $\text{NO}_2 + \text{NO}$  ;
- (c)  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ .

The first reaction (a) occurs when liquid nitrogen trioxide is vaporised after having been dried as completely as possible. Vapour density measurements showed that dissociation into equal volumes of nitrogen trioxide, nitrogen peroxide, and nitric oxide was complete at  $140^{\circ}\text{C.}$  At the same time, however, there would be present a few  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$  and  $\text{NO}$  molecules, (b), which was due to incomplete drying. These "wet" molecules would take no part in the first reaction, neither would they combine to form nitrogen trioxide. Association of  $\text{NO}_2$  to  $\text{N}_2\text{O}_4$  molecules will occur if sufficient moisture is present, (c).

Dry liquid nitrogen trioxide is blue, but if moisture is present a green liquid results, owing to the mixture of wet  $\text{NO}_2$  molecules with the blue trioxide. At very low temperatures all specimens of trioxide become blue even if slightly wet because of the complete association of any wet  $\text{NO}_2$  molecules to give colourless  $\text{N}_2\text{O}_4$ .

In the gaseous state both  $\text{N}_4\text{O}_6$  and  $\text{N}_2\text{O}_3$  are colourless when pure.

**Chemical Properties of Nitrogen Trioxide.**—Nitrogen trioxide is oxidised completely to the peroxide with air or oxygen when in the gaseous state.<sup>6</sup> In the liquid state oxidation only occurs if the temperature is below  $-100^{\circ}\text{C.}$ <sup>2</sup>

In many of its reactions nitrogen trioxide reacts as a mixture of the peroxide and nitric oxide. Some metals are converted into their oxides with the formation of nitric oxide or nitrogen, according to whether they are at a red heat or more strongly ignited. Hydrogen sulphide is oxidised to sulphur, and sulphur dioxide, in the presence of moisture, undergoes the same reactions as with nitrous acid, but no reaction occurs when quite dry. Sulphur trioxide in carbon bisulphide solution forms sulpho-nitrous anhydride,  $(\text{SO}_3)_5(\text{N}_2\text{O}_3)_3$ .

<sup>1</sup> Baker, *loc. cit.* See p. 164.

<sup>2</sup> Francesconi and Sciacca, *Gazzetta*, 1904, 34, (i), 447.

<sup>3</sup> Baume and Roberts, *Compt. rend.*, 1919, 169, 968.

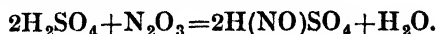
<sup>4</sup> Geuther, *Annalen*, 1888, 245, 96.

<sup>5</sup> Jones, *Trans. Chem. Soc.*, 1914, 105, 2310.

<sup>6</sup> Porschaew, *Zeitsch. anorg. Chem.*, 1894, 7, 214; Holwech, *Zeitsch. angew. Chem.*, 1908, 21, 2131.



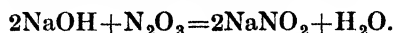
Concentrated sulphuric acid absorbs nitrogen trioxide completely with the formation of nitrosyl-sulphuric acid :



Nitrogen trioxide mixes with a small amount of water at  $0^\circ \text{C}$ . to give a bluish-green liquid which effervesces with the liberation of nitric oxide, and contains both nitric and nitrous acids. With a large excess of water no evolution of gas occurs, and the relatively dilute solution, which contains nitrous acid, is fairly stable.<sup>1</sup>

According to Baker,<sup>2</sup> the trioxide does not dissolve as such in water, but sinks to the bottom and decomposes into nitric oxide and nitrogen peroxide, which latter oxide dissolves in the water to form both nitric and nitrous acids.

Dry sodium and potassium hydroxides completely absorb nitrogen trioxide, with the exclusive formation of nitrite :



If there is any moisture present, however, decomposition into nitrous and nitric acids occurs first, and neutralisation takes place with the formation of nitrate as well as nitrite, but a certain amount of the nitrous acid decomposes, with evolution of nitric oxide, before neutralisation.<sup>3</sup>

Chloroform forms a blue additive compound with nitrogen trioxide at  $-20^\circ \text{C}$ ., which decomposes at ordinary temperatures with the evolution of nitric oxide and nitrogen peroxide.<sup>4</sup>

#### NITROGEN TETROXIDE (NITROGEN "PER"-OXIDE).

**History.**—The formation of brown nitrous fumes under varying conditions was noted by many earlier experimenters. Thus Hales<sup>5</sup> in 1727 obtained these fumes by mixing nitric oxide (nitrous air) with air. Scheele<sup>6</sup> in 1777 mentions their removal from fuming nitric acid by heat; and in the same year Priestley<sup>7</sup> investigated the gas obtained by the action of nitric acid on many metals, as well as the preparation by oxidising nitric oxide. Priestley proposed a method for testing "the goodness of common air" by mixing air with excess of nitric oxide over water. He was the first to notice a darkening of colour when the gas was heated,<sup>8</sup> which we now know of course was due to dissociation of the tetroxide molecules.

Cavendish<sup>9</sup> in 1781 showed the formation of nitrous fumes when electric sparks are passed through air, and these fumes dissolved in water to form nitric acid. Davy<sup>10</sup> in 1800 attempted to determine the composition of nitrogen peroxide by mixing nitric oxide and oxygen and absorbing the product in water, but his results were not very

<sup>1</sup> Marchlewski, *Zeitsch. anorg. Chem.*, 1894, 5, 88.

<sup>2</sup> Baker, *Trans. Chem. Soc.*, 1907, 91, 1862.

<sup>3</sup> Klinger, *Zeitsch. angew. Chem.*, 1914, 27, 7.

<sup>4</sup> Saposchnikoff, *J. Russ. Chem. Ges.*, 1900, 32, 375.

<sup>5</sup> Hales, *Vegetable Statics*, 1727, p. 71.

<sup>6</sup> Priestley, *Alcmbic Club Reprints*, VIII, 198.

<sup>7</sup> Priestley, *Experiments on Air*, 1777, III, 184.

<sup>8</sup> Priestley, *ibid.*, 1777, III, 186.

<sup>9</sup> Cavendish, *ibid.*, 1781, Part I, 188; Part II, 189.

<sup>10</sup> Davy, *Works*, III, 15.

successful. A more accurate method was adopted by Gay-Lussac<sup>1</sup> in 1816, who measured the contraction which occurred when nitric oxide and oxygen were mixed over mercury. He concluded that 2 volumes of nitric oxide and 1 volume of oxygen produced 1 volume of nitrogen peroxide. This result is approximately true at ordinary temperatures where there is a preponderance of  $\text{N}_2\text{O}_4$  molecules.

**Preparation.**—1. Nitrogen tetroxide is ultimately obtained by mixing nitric oxide and oxygen in the proportions of 2 : 1 by volume.<sup>2</sup> Complete mixing is obtained by passing the gases through a tube containing broken glass, and the tetroxide may be condensed to a colourless crystalline mass in a U-tube kept at  $-20^\circ \text{C}.$  :



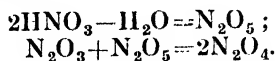
2. The nitrates of the heavy metals decompose on heating into a mixture of nitrogen tetroxide and oxygen. The former may be condensed by passing through a U-tube immersed in a freezing mixture :



3. The reduction of nitric acid by arsenious oxide is one of the most convenient methods for preparing quantities of nitrogen tetroxide :<sup>3</sup>



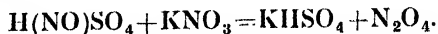
With nitric acid of specific gravity 1.40 or 1.45 a certain amount of nitrogen trioxide is also produced. Cundall's method<sup>4</sup> is to add a cooled mixture containing 315 grams of fuming nitric acid and 150 grams of sulphuric acid to 250 grams of coarsely powdered arsenious oxide in a litre flask. The reaction commences slightly above room temperature, and requires external cooling. A reflux condenser is fitted to effect preliminary cooling of the gas, which is passed through a U-tube containing phosphoric oxide, and then condensed to a liquid in a U-tube surrounded by ice and salt. The distillation is stopped as soon as the liquid in the flask turns a green colour; all joints are glass-joints, cork and rubber being quickly attacked. Purification of the liquid nitrogen tetroxide is effected by treating with fuming nitric acid and excess phosphoric oxide :



The liquid is finally distilled, passed over powdered arsenious oxide, and reliquefied by cooling.

4. Fractional distillation of fuming nitric acid gives nitrogen tetroxide contaminated with small amounts of nitric acid and nitrogen trioxide.<sup>5</sup>

5. Nitrosyl-sulphuric acid warmed with potassium nitrate evolves nitrogen tetroxide :<sup>6</sup>



<sup>1</sup> Gay-Lussac, *Ann. Chim.*, 1816, **1**, 401.

<sup>2</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1816, [2], **1**, 394; Pélignet, *ibid.*, 1841, [3], **2**, 58; Dulong, *ibid.*, 1816, [2], **2**, 317.

<sup>3</sup> Hasenbach, *J. prakt. Chem.*, 1871, [2], **4**, 1.

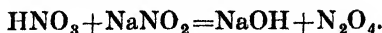
<sup>4</sup> Cundall, *Trans. Chem. Soc.*, 1891, **59**, 1076.

<sup>5</sup> Mitscherlich, *Lehrbuch*, **1**, 345.

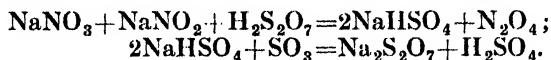
<sup>6</sup> Girard and Pabst, *Bull. Soc. chim.*, 1878, (ii), **30**, 531.

6. A number of methods of preparation from nitrites have been devised :

(i) The action of nitric acid upon a nitrite : <sup>1</sup>

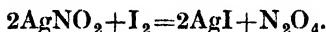


(ii) The action of fuming sulphuric acid upon a fused mixture of sodium nitrate and nitrite, to which sufficient sodium bisulphate has been added to fix free sulphur trioxide : <sup>2</sup>



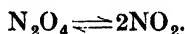
(iii) Nitrogen tetroxide is produced when fused alkali nitrites are electrolysed. <sup>3</sup>

(iv) Iodine reacts with silver nitrite with the liberation of nitrogen tetroxide : <sup>4</sup>



7. A good yield of nitrogen tetroxide is obtained by passing a mixture of air and steam through a thin porcelain tube maintained at 1600° C. The hydrogen produced diffuses through the tube, and the rate of diffusion is accelerated by raising the pressure inside the tube and lowering the pressure outside. <sup>5</sup>

**The Physical Properties of Nitrogen Tetroxide.**—Nitrogen tetroxide at ordinary temperatures is a brown gas with a characteristic smell, and is toxic even when inhaled in small quantities. The density shows a considerable variation with temperature owing to the dissociation :



The variation of density (referred to air = 1) with temperature is given in the following table :—

Temperature, ° C.	Density.	Authority.	Temperature, ° C.	Density.	Authority.
4.2	2.588	Playfair and Wanklyn, <i>Trans. Roy. Soc. Edin.</i> , 1861, 22, 111, 441.	49.6	2.27	Deville and Troost, <i>Compt. rend.</i> , 1867, 64, 237.
11.3	2.645		60.2	2.08	
24.5	2.520		70.0	1.92	
97.5	1.783		80.6	1.80	
28	2.70	Muller, <i>Annalen</i> , 1862, 122, 1.	90.0	1.72	
32	2.65		100.1	1.68	
52	2.26		111.3	1.65	
70	1.95		121.5	1.63	
79	1.84	Deville and Troost, <i>Compt. rend.</i> , 1867, 64, 237.	135	1.60	
26.7	2.65		154	1.58	
35.4	2.53				
39.8	2.46				

<sup>1</sup> Girard and Pabst, *Bull. Soc. chim.*, 1878, (ii), 30, 531.

<sup>2</sup> Winan, *German Patent*, 193696 (1908).

<sup>3</sup> Bogorodski, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 703.

<sup>4</sup> Neelmayer, *Ber.*, 1904, 37, 1386.

<sup>5</sup> *Westdeutsche Thomasphosphatwerke, German Patent*, 182297 (1908).

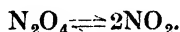
These data permit the calculation of the degree of dissociation " $\alpha$ " from the relation :

$$1 + \alpha = \frac{\Delta}{D}, \text{ i.e. } \alpha = \frac{\Delta - D}{D};$$

in which  $\Delta$  is the theoretical density of  $\text{N}_2\text{O}_4$  (e.g. relative to air) and  $D$  is that observed.

**Refractivity of Nitrogen Dioxide.**—Since this gas shows a strong selective absorption in regions of shorter wave-length, a red line at  $\lambda = 6438 \text{ \AA.}$  was chosen when the density and refractivity are both reduced to N.T.P. For  $\text{NO}_2$ ,  $(n-1) = 0.0005087$ ; for  $\text{N}_2\text{O}_4$ ,  $(n-1) = 0.001123$ .

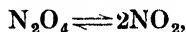
**Dissociation of Nitrogen Tetroxide.**—Solid colourless nitrogen tetroxide apparently consists of  $\text{N}_2\text{O}_4$  molecules entirely, but the liquid contains some  $\text{NO}_2$  molecules, and the concentration of these latter increases with rise of temperature and is followed by the deepening of colour. Thus, between the temperatures of  $-10^\circ$  to  $26^\circ \text{ C.}$  the liquid gradually becomes a deeper yellow, until at the boiling-point ( $26^\circ \text{ C.}$ ) it assumes a distinctly orange colour. The reddish-brown vapour continues to show an increasing deepening of colour, until at a temperature of  $140^\circ \text{ C.}$  the gas is almost black owing to its complete dissociation into the single  $\text{NO}_2$  molecules :



The following table gives the percentages of  $\text{NO}_2$  molecules present at varying temperatures which have been calculated from the density determinations :—<sup>2</sup>

Temperature, $^\circ \text{ C.}$	Density ( $\text{H}_2 = 2$ ).	$\text{NO}_2$ Molecules (per cent.).
26.7	76.6	20
60.2	60.2	50.04
100.1	48.6	79.23
135.0	46.2	98.96
140.0	46.0	100.00

The dissociation constant of the equilibrium,



is given by

$$K = \frac{[\text{N}_2\text{O}_4]^{\frac{1}{2}}}{[\text{NO}_2]},$$

and the variation of this constant with temperature is given in the following table :—<sup>3</sup>

Temperature, $^\circ \text{ C.}$	0.0	18.3	49.9	73.6	99.8
Dissociation constant $K$ .	8.060	3.710	1.116	0.544	0.273

<sup>1</sup> C. & M. Cuthbertson, *Proc. Roy. Soc.*, 1913, (A) 89, 361.

<sup>2</sup> Deville and Troost, *loc. cit.*

<sup>3</sup> Schreber, *Zeitsch. physikal. Chem.*, 1897, 24, 651.

Fig. 18 shows these results graphically.

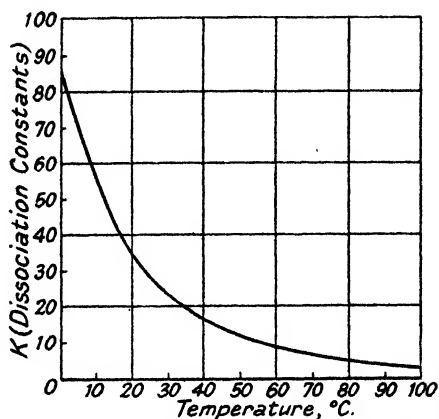


FIG. 18.—Dissociation constants of nitrogen tetroxide.

The thermal dissociation<sup>1</sup> of nitrogen dioxide ( $\text{NO}_2$ ) into nitric oxide and oxygen above  $150^\circ \text{C.}$  under different temperatures and pressures has been studied, with the following results:—

Temperature, °C.	Pressure, mm.	Density.	Percentage of $\text{NO}_2$ Dissociated.
130	718.5	1.600	
184	754.6	1.551	5
279	737.2	1.493	13
494	742.5	1.240	56.5
620	760.0	1.060	100.0

The variation in the density with the pressure at one temperature, namely,  $49.7^\circ \text{C.}$  (see table below), indicates, as was to be expected, an increase in the dissociation with decreasing pressure, since in the dissociation the number of molecules derived from a given weight of the gas is increased, and this tends to increase the pressure. The expression, which should be constant, is

$$\frac{4a^2P}{(1+a)(1-a)RT}$$

When  $a$  is expressed in terms of the densities, and the whole expression is divided by constants which are independent of the dissociation, *i.e.*  $\Delta$  and  $R$ , and also of the temperature (since this is constant), the equilibrium constant is represented by

$$K' = \frac{(\Delta - D)^2 P}{2D - \Delta}.$$

<sup>1</sup> Richardson, *Trans. Chem. Soc.*, 1887, 51, 397.

Dissociation and pressure at  $49.7^{\circ}\text{C}.$ :<sup>1</sup>

P (mm.) =	0	26.8	93.75	182.69	261.37	497.75
Density =	(1.590)	1.663	1.788	1.894	1.963	2.144
$\alpha$ =	1.000	0.93	0.789	0.690	0.630	0.493
K' =	106	106	112	124	130	121

Thus, under these conditions, the gas is nearly 50 per cent. dissociated at a pressure of 497.75 mm.

Fig. 19 shows the dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$ , and of  $\text{NO}_2$  into nitric oxide and oxygen.<sup>2</sup>

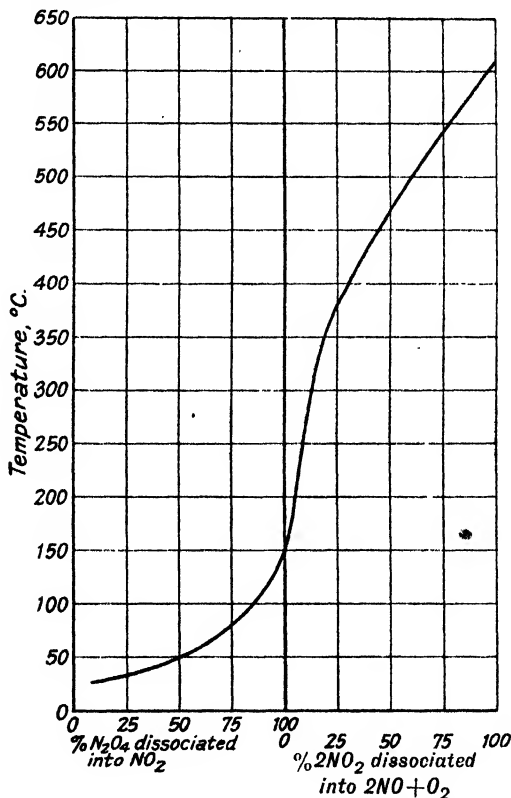


FIG. 19.—Thermal dissociation of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .

*Specific Heats of Nitrogen Tetroxide.*—The specific heat at constant pressure of nitrogen tetroxide varies considerably with temperature, owing to dissociation. It has been pointed out,<sup>3</sup> that the determinations of Berthelot and Ogier<sup>4</sup> took no account of barometric fluctuations over different ranges, and further, that the heat of dissociation was included in the specific heat. The following table<sup>3</sup> gives results obtained by use of a constant flow method which obviated the necessity

<sup>1</sup> E. and L. Natanson, *Wied. Annalen*, 1885, 24, 454; 1886, 27, 606.

<sup>2</sup> Richardson, *loc. cit.*

<sup>3</sup> McCollum, *J. Amer. Chem. Soc.*, 1927, 49, 28.

<sup>4</sup> Berthelot and Ogier, *Ann. Chim. Phys.*, 1883, [5], 30, 385.

of measuring the temperature change and also the water equivalent of the calorimeter :—

Temperature, ° C.	Total Heat Capacity.	Heat of Dissociation.	Specific Heat.
33.73	126	114.6	11.4
41.00	146	134.2	12.0
44.00	154	141.6	12.0
55.03	176	160.8	15.2
60.90	178	163.3	14.7
63.33	179	162.4	16.6
70.70	168	153.1	14.9
80.89	143	126.9	16.1
97.51	93	75.5	17.5

These results show that the specific heat of nitrogen tetroxide is very small compared with the heat of dissociation, and also that the value  $C_p$  for  $N_2O_4$  is slightly greater than  $C_p$  for  $NO_2$ .

The following table gives the results of a number of observers which have been collected and recalculated :—<sup>1</sup>

Temperature, ° C.	Pressure, mm. Hg.	Percentage Dissociation.	$C_p$	$C_v$	$\gamma = \frac{C_p}{C_v}$
25	599	19.51	19.98	17.92	1.1154
23	304	25.00	16.96	14.93	1.1359
23	106	40.54	13.70	11.69	1.1712
22	218	28.24	17.19	15.17	1.1330
21	500	11.21	22.22	20.17	1.1020

The heat of dissociation of gaseous nitrogen tetroxide has been given by various observers as  $-13,000$ ,<sup>2</sup>  $-13,050$ ,<sup>2</sup>  $-12,900$ ,<sup>3</sup>  $-13,920$ ,<sup>4</sup> and  $-13,132$ <sup>5</sup> calories respectively.

The heat of formation of nitrogen tetroxide (containing 9 per cent. of  $NO_2$ ) from  $2N + 4O \rightleftharpoons N_2O_4$ , is  $-3900$  calories.

In the case of completely dissociated  $NO_2$  the value is  $-8125$  calories, and with completely associated  $N_2O_4$  (liquid),  $-2650$  calories.<sup>6</sup>

The heat of formation of liquid nitrogen tetroxide ( $NO_2 = 46$  grams) is  $-2200$  calories.<sup>7</sup>

The heat of vaporisation at  $18^\circ C.$  is  $-4300$  calories.<sup>7</sup> The latent heat of fusion varies from  $-32.2$  to  $-37.2$  calories per gram, which corresponds to  $-2960$  to  $-3420$  calories per mol. of  $N_2O_4$ . The value

<sup>1</sup> Partington and Shilling, *The Specific Heats of Gases* (Benn, 1924).

<sup>2</sup> Swart, *Zeitsch. physikal. Chem.*, 1891, 7, 124.

<sup>3</sup> van 't Hoff, *Vorlesungen*, I, 1901, p. 140.

<sup>4</sup> Boltzmann, *Wied. Annalen*, 1884, 22, 68.

<sup>5</sup> Schreber, *Zeitsch. physikal. Chem.*, 1897, 24, 660.

<sup>6</sup> Thomsen, *Thermochemische Untersuchungen*, 1906, p. 163.

<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1875, (v), 6, 145.

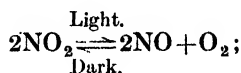
calculated from the depression of the freezing-point is  $-33.7$  calories per gram.<sup>1</sup> The thermal conductivity for  $\text{NO}_2$  at  $150^\circ \text{C}$ . is  $0.0033$ .<sup>2</sup>

The thermal expansion of liquid nitrogen tetroxide is very regular,<sup>3</sup> as is evident from the following data :—

Temperature, $^\circ \text{C}$ . .	0	5	10	15	20
Volume . . .	1.0000	1.00789	1.01573	1.02370	1.03196

Molecular weight determinations in acetic acid show that liquid nitrogen tetroxide is not polymerised beyond the  $\text{N}_2\text{O}_4$  molecule.<sup>4</sup>

The effect of ultra-violet light on nitrogen tetroxide has been studied,<sup>5</sup> and it is found that an increase in pressure occurs which is not due to heating effect of the absorbed light. This pressure increase is due, firstly, to a photochemical equilibrium in the system :



while in the second place there is a heating effect due to the recombination of nitric oxide and oxygen as well as by absorbed radiation.

The refractive index of gaseous nitrogen tetroxide is  $1.000503$  at  $36^\circ \text{C}$ .<sup>6</sup> (See also p. 169).

The spectrum of nitrogen tetroxide has been studied by Bell,<sup>7</sup> who found that there was an increase in the general and selective absorption with rise of temperature. The conclusion that the absorption spectrum is due entirely to  $\text{NO}_2$  molecules is supported by the fact that no absorption is shown by liquid nitrogen tetroxide a few degrees below  $0^\circ \text{C}$ .

**Liquid Nitrogen Tetroxide.**—As mentioned in the preparation, nitrogen tetroxide is easily liquefied at atmospheric pressure by condensing the gas in a freezing mixture.<sup>8</sup> The liquid is pale yellow in colour and boils at  $22^\circ \text{C}$ .<sup>9</sup>

The variation of the density of liquid nitrogen tetroxide with temperature is shown in the following table :—<sup>10</sup>

Temperature, $^\circ \text{C}$ . .	-5	-4	-2	-1	0	+5	+10	+15	+21.6
Density . . .	1.5035	1.5030	1.5020	1.5000	1.4935	1.4880	1.4770	1.4740	1.4398

The density of liquid nitrogen tetroxide between  $0^\circ$  and  $21.5^\circ \text{C}$ . may be represented by the equation <sup>11</sup>

$$D_t' = 1.490 - 0.00215t.$$

The vapour pressure of liquid nitrogen tetroxide at different temperatures is given in the following table :—<sup>12</sup>

<sup>1</sup> Ramsay, *Zeitsch. physikal. Chem.*, 1890, 5, 221.

<sup>2</sup> Feliciani, *Physikal. Zeitsch.*, 1905, 6, 20.

<sup>3</sup> Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141.

<sup>4</sup> Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 12, 433.

<sup>5</sup> Norrish, *ibid.*, 1927, 131, 761.

<sup>6</sup> Dulong, *Zeitsch. physikal. Chem.*, 1901, 36, 322.

<sup>7</sup> Bell, *Amer. Chem. J.*, 1885, 7, 32. See also Hasselberg, *Zeitsch. anal. Chem.*, 1879, 18, 571; Kundt, *Pogg. Annalen*, 1870, 141, 157; Gernez, *Compt. rend.*, 1872, 74, 465.

<sup>8</sup> Gay-Lussac, *Ann. Chim. Phys.*, 1816, 1, 405.

<sup>9</sup> Odds, *Gazzetta*, 1915, 45, (i), 413.

<sup>10</sup> Geuther, *Annalen*, 1888, 245, 96; Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141.

<sup>11</sup> Pascal and Garnier, *Bull. Soc. chim.*, 1919, (iv), 25, 309.

<sup>12</sup> Scheffer and Treub, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 536.



Temperature, ° C.	Vapour Pressure, mm. Hg.	Temperature, ° C.	Vapour Pressure, mm. Hg.
-23.0	70	15.0	565
-10.0	146	21.45	770
- 6.9	180	27.4	1007
- 0.6	256	39.0	1668
+ 7.7	293	43.2	1982

The critical temperature of nitrogen tetroxide is  $158.2^{\circ}\text{C.}$ , and the critical pressure  $100 \pm 2$  atmospheres.<sup>1</sup>

The freezing-point curve of nitrogen tetroxide and trioxide mixtures is shown in fig. 20.<sup>2</sup> Solid tetroxide or trioxide separates according to

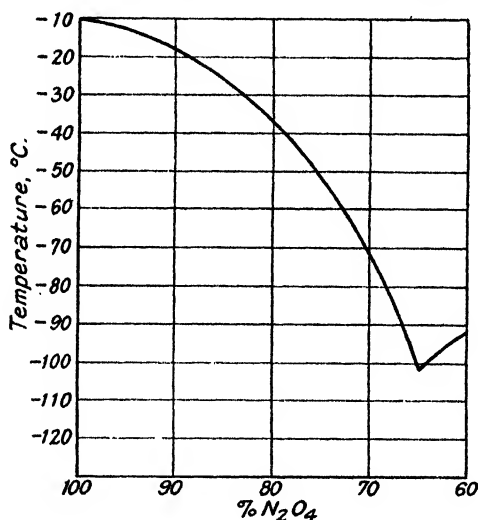


FIG. 20.—Freezing-point curve of nitrogen tetroxide and nitrogen trioxide mixtures.

the richness of the mixture, and eventually a eutectic mixture separates at  $-112^{\circ}\text{C.}$  which has the composition 7.8 per cent.  $\text{N}_2\text{O}_4$  and 92.2 per cent.  $\text{N}_2\text{O}_3$  (corresponding to 63.6 per cent.  $\text{NO}_2$  and 36.4 per cent.  $\text{NO}$ ). No other compound exists, therefore, between  $-10^{\circ}$  and  $-112^{\circ}\text{C.}$

**Solid Nitrogen Tetroxide.**—Solid nitrogen tetroxide exists in the form of colourless crystals, the melting-point of which is given variously as  $-10.1^{\circ}$ ,<sup>3</sup>  $-10.5^{\circ}$ ,<sup>4</sup>  $-10.8^{\circ}$ ,<sup>5</sup> and  $-10.95^{\circ}$ .<sup>6</sup>

The variation of the vapour pressure with the temperature is given in the following table :—<sup>4</sup>

<sup>1</sup> Scheffer and Treub, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 166.

<sup>2</sup> Wittorf, *Zeitsch. anorg. Chem.*, 1904, 41, 85.

<sup>3</sup> Ramsay, *Zeitsch. physikal. Chem.*, 1890, 5, 221.

<sup>4</sup> Egerton, *Trans. Chem. Soc.*, 1914, 105, 647.

<sup>5</sup> Scheffer and Treub, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 536.

<sup>6</sup> Bruni and Berti, *Atti R. Accad. Lincei*, 1900, (v), 9, i, 321.

Temperature, ° C.	Vapour Pressure, mm. Hg.	Temperature, ° C.	Vapour Pressure, mm. Hg.
—30	39.240	— 70	0.1510
—40	9.770	— 80	0.0860
—50	2.440	— 90	0.0098
—60	0.605	—100	0.0023

The above values are obtained from the equation

$$\log p = 14.9166 + \theta(0.0604).$$

It would seem that solid nitrogen tetroxide consists entirely of  $\text{N}_2\text{O}_4$  molecules.

**Chemical Properties of Nitrogen Tetroxide.**—Nitrogen tetroxide is not inflammable, neither does it support the combustion of feebly burning substances, *e.g.* a taper is extinguished. At higher temperatures, however, it is a powerful oxidising agent, owing to its decomposition into oxygen and nitrogen. Thus, freely burning carbon, sulphur, and phosphorus are converted into their oxides; <sup>1</sup> carbon monoxide burns to the dioxide, and hydrogen sulphide to sulphur, with formation of nitric oxide. Hydrogen mixed with nitrogen tetroxide, and passed over platinum,<sup>2</sup> copper, or nickel,<sup>3</sup> reduces the tetroxide to ammonia.

Potassium, which burns with a red flame in  $\text{N}_2\text{O}_4$ , sodium, lead, and mercury are all oxidised to the nitrates, with formation of nitric oxide. Iron, cobalt, and tin, heated to 500° C., are converted into oxides, while many lower metallic oxides are further oxidised at this temperature in the gas. Calcium oxide yields the nitrate when heated to 300°–400° C.,<sup>4</sup> while barium oxide at 200° C. produces both nitrate and nitrite.<sup>5</sup>

Certain metals, such as copper, nickel, and cobalt, when in the finely divided condition, absorb both gaseous and liquid nitrogen tetroxide, with the formation of unstable products, which decompose into their constituents on heating, and react vigorously with water, evolving nitric oxide and leaving a solution containing nitrites and nitrates.<sup>6</sup> These so-called “nitro-metals” were considered to be definite compounds with formulæ such as  $\text{Cu}_2\text{NO}_2$ ,  $\text{Ni}_4\text{NO}_2$ ,  $\text{Co}_2\text{NO}_2$ . Recent work,<sup>7</sup> however, with the supposed “nitro-copper” has shown it to be merely an adsorption complex of  $\text{NO}_2$  in  $\text{Cu}_2\text{O}$ . The amount of nitrogen peroxide absorbed by the copper is variable, and the first reaction is the oxidation of the copper to cuprous oxide :



The cuprous oxide then reabsorbs the tetroxide, producing a complex  $y\text{NO}_2.x\text{Cu}_2\text{O}$ .

<sup>1</sup> Dulong, *Ann. Chim. Phys.*, 1816, [2], 2, 317.

<sup>2</sup> Kuhlmann, *Annalen*, 1839, 29, 272.

<sup>3</sup> Sabatier and Senderens, *Compt. rend.*, 1902, 135, 278.

<sup>4</sup> Schloesing, *English Patent*, 22119 (1913).

<sup>5</sup> Dulong, *Annalen*, 1862, 18, 122.

<sup>6</sup> Sabatier and Senderens, *Compt. rend.*, 1892, 115, 236; *Ann. Chim. Phys.*, 1896, (vii), 7, 348.

<sup>7</sup> Partington, *Trans. Chem. Soc.*, 1924, 125, 72, 663.

Cuprous oxide is capable of absorbing 30 per cent. of nitrogen tetroxide gas, but the liquid has no visible action.

Nitrogen tetroxide resembles nitric oxide in forming additive compounds with metallic halides. A number of such compounds have been investigated,<sup>1</sup> typical examples of which are  $\text{BiCl}_3 \cdot \text{NO}_2$ ,  $\text{SnCl}_4 \cdot \text{NO}_2$ ,  $\text{FeCl}_3 \cdot \text{NO}_2$ ,  $4\text{FeCl}_2 \cdot \text{NO}_2$ ,  $4\text{FeBr}_2 \cdot \text{NO}_2$ .

Dry oxygen has no action upon nitrogen tetroxide, but in the presence of water, oxidation to nitric acid occurs. Ozone oxidises the tetroxide to the pentoxide.

Nitrogen tetroxide reacts with small quantities of water to produce nitrous and nitric acids :



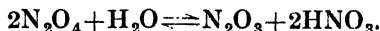
The subsequent decomposition of the nitrous acid depends upon the amount of water present. If the latter is small, then the following reaction occurs :—



An excess of water, however, results in the production of nitric oxide and nitric acid : <sup>2</sup>

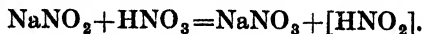


Well-cooled liquid nitrogen peroxide added to a small quantity of water produces two distinct layers. The upper light green layer consists of nitric acid with nitric oxide, while the lower deep blue layer is chiefly nitrogen trioxide :



If oxygen is bubbled through these two layers, the top layer becomes orange-yellow, and contains nitric acid of concentration 95 to 99 per cent., while the bottom layer consists of nitrogen tetroxide with 5 to 10 per cent. of nitric acid.<sup>3</sup>

Solutions of potassium and sodium hydroxides readily absorb nitrogen peroxide, with the formation of nitrate and nitrite. Actually, decomposition by the water present first occurs, and the neutralisation of the nitric and nitrous acids then follows. Some nitrous acid, however, always escapes neutralisation, and decomposes with evolution of nitric oxide. Maximum absorption occurs when the concentration of the alkali is about 1.5N. A 4N solution absorbs to the same extent as water, and stronger solutions are less effective than pure water.<sup>4</sup> A commercially pure alkaline nitrate is produced by passing in nitrogen peroxide in excess of the quantity required for neutralisation to nitrite and nitrate. The nitrite is converted into nitrate by the nitric acid formed by the action of the peroxide on the water, accompanied by evolution of nitric oxide :



Nitrogen peroxide is absorbed by aqueous solutions of sodium and potassium carbonates less vigorously than the caustic alkalies. Nitrate

<sup>1</sup> Thomas, *Compt. rend.*, 1895, 120, 447 ; 1895, 121, 128, 204 ; 1896, 123, 443 ; 1897, 124, 366 ; *Ann. Chim. Phys.*, 1898, [7], 13, 145.

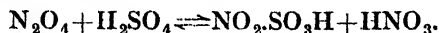
<sup>2</sup> Saposchnikoff, *Chem. Zentr.*, 1900, (ii), 708 ; 1901, (ii), 330.

<sup>3</sup> Friderich, *English Patent*, 319 (1911).

<sup>4</sup> Webb, *Absorption of Nitrous Gases* (Arnold, 1923).

and nitrite are produced with evolution of carbon dioxide less vigorously than when using caustic alkalies.

Concentrated sulphuric acid absorbs nitrogen peroxide with the formation of nitrosyl-sulphuric acid : <sup>1</sup>



This reaction is reversible, and proceeds from right to left with rise of temperature.<sup>2</sup>

Sulphur dioxide and sulphur trioxide give a number of complex substances when acted upon by nitrogen peroxide under varying conditions.<sup>3</sup> The composition of these compounds has not been elucidated, but it is stated that the chief product of liquid nitrogen tetroxide and sulphur dioxide is  $\text{O}(\text{SO}_2\text{—ONO})_2$ , which may be regarded as the anhydride of nitrosyl-sulphuric acid.<sup>3</sup>

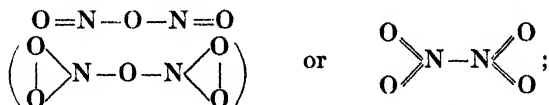
Both dilute and concentrated nitric acid absorb nitrogen peroxide,<sup>4</sup> and the maximum amount absorbed by the concentrated acid is 42.5 per cent. by weight. This corresponds to the formula  $\text{N}_2\text{O}_5 \cdot \text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}^5$ .

Solid nitrogen tetroxide and liquid ammonia at  $-80^\circ \text{C}$ . react with explosive violence, but with gaseous ammonia at  $-20^\circ \text{C}$ . a less vigorous reaction occurs, with the formation of a number of products such as nitrogen, nitric oxide, water, ammonium nitrite and nitrate.<sup>6</sup>

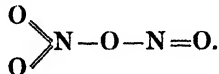
Nitrogen peroxide is a useful nitrating agent for a large number of organic compounds.<sup>7</sup>

Liquid nitrogen peroxide is a useful solvent for cryoscopic determinations of a number of organic compounds, the molecular elevation of the boiling-point being  $13.7^\circ \text{C}$ . and the molecular depression of the freezing-point  $41^\circ \text{C}$ .<sup>8</sup>

**Constitution.**—Various constitutions have been assigned to nitrogen peroxide both in the  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  states. In  $\text{N}_2\text{O}_4$  both nitrogen atoms may be assumed to be tervalent or quinquevalent :



or possibly each of the nitrogen atoms exhibits a different valency :



This formula best explains the mixed anhydride character of the tetroxide as exhibited by its reaction with water to form nitrous and nitric acids.

Difficulty is experienced, however, in the case of  $\text{NO}_2$ . Here the

<sup>1</sup> Weber, *Pogg. Annalen*, 1867, 130, 277 ; Lunge, *Ber.*, 1879, 12, 1058.

<sup>2</sup> Lunge and Weintraub, *Zeitsch. angew. Chem.*, 1899, 12, 417.

<sup>3</sup> Weber, *loc. cit.* ; and 1864, 123, 339 ; Hasenbach, *J. prakt. Chem.*, 1871, [2], 4, 4 ; Friedburg, *Chem. News*, 1883, 47, 52.

<sup>4</sup> Lunge and Marchlewsky, *Zeitsch. angew. Chem.*, 1912, 25, 10.

<sup>5</sup> Pascal and Garnier, *Bull. Soc. chim.*, 1919, (iv), 25, 309.

<sup>6</sup> Besson and Rosset, *Compt. rend.*, 1906, 142, 633.

<sup>7</sup> Wieland, *Ber.*, 1921, 54, 1776.

<sup>8</sup> Ramsay, *Zeitsch. physikal. Chem.*, 1900, 5, 221 ; Bruni and Berti, *Gazzetta*, 1900, 30, (ii), 151 ; Frankland and Farmer, *Trans. Chem. Soc.*, 1901, 79, 1356.

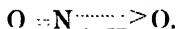
nitrogen atom must either be trivalent or quinquivalent with a free valency, as in



or else the nitrogen atom must function in a quadrivalent capacity : <sup>1</sup>



In accordance with the theories of valency stated on p. 14, the nitrogen atom is quadricovalent with one mixed bond, thus :



**Detection and Estimation.**—Nitrogen tetroxide can be readily detected by its colour, odour, action on starch iodide solution, etc.

The estimation is accompanied by difficulties which have been mentioned in connection with nitric oxide (p. 159). The absorption by aqueous caustic alkalis to form nitrite and nitrate may be used quantitatively :

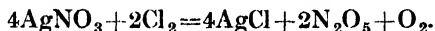


The formation of nitrosyl-sulphuric acid occurs by absorption in 85 to 95 per cent. sulphuric acid, and this may be estimated by titration with potassium permanganate.

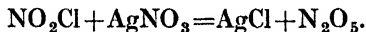
#### NITROGEN PENTOXIDE.

**History.**—Deville<sup>2</sup> first isolated this oxide by decomposing silver nitrate with dry chlorine. Meyer<sup>3</sup> obtained it later from nitric acid by dehydrating with phosphorus pentoxide.

**Preparation.**—1. Dry chlorine reacts with silver nitrate at 95° C., and as soon as the action has started the mixture is cooled to 50°–60° C. The nitrogen pentoxide evolved is separated from the oxygen by condensing in a U-tube immersed in a freezing mixture. No corks or rubber joints may be used owing to the corrosive action of the gas : <sup>2</sup>



It is also produced by the reaction between nitryl chloride and silver nitrate :



2. The most convenient method is by the dehydration of nitric acid.<sup>4</sup> This is first obtained pure by repeated distillation with concentrated sulphuric acid, and bubbling dry air through the final distillate in order to remove oxides of nitrogen. 200 grams of this “white fuming acid” are put into a 2-litre flask with a side arm at right angles to the neck, and 400 grams of phosphorus pentoxide are slowly added during cooling until pasty. The flask is then attached by means of

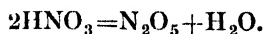
<sup>1</sup> See Piloty and Schwerin, *Ber.*, 1901, 34, 1863, 2354; Divers, *Trans. Chem. Soc.*, 1904, 84, 110.

<sup>2</sup> Deville, *Ann. Chim. Phys.*, 1849, (iii), 28, 241.

<sup>3</sup> Meyer, *Ber.*, 1889, 22, 23.

<sup>4</sup> Meyer, *loc. cit.*; Daniels, *J. Amer. Chem. Soc.*, 1920, 42, 1131.

sealing-wax to three wash-bottles, the first containing glass-wool and phosphorus pentoxide, and the others being empty, and immersed in a freezing mixture of ice and salt. The flask is heated on a water-bath to 60°–70° C. and a slow stream of air (dried by concentrated sulphuric acid) is passed through the paste. The nitrogen pentoxide collects in the wash-bottles as a slightly yellow brittle solid :



3. Nitrogen trioxide and nitrogen tetroxide are both oxidised by ozone to nitrogen pentoxide.<sup>1</sup>

4. A mixture of nitrogen and oxygen can be converted into nitrogen pentoxide by means of the silent electric discharge in the presence of ozone.<sup>2</sup>

**Physical Properties.**—Solid nitrogen pentoxide exists in colourless, transparent rhombic plates, melting-point 29·5° C.,<sup>3</sup> and specific gravity 1·63.<sup>3</sup> The yellow colour which develops at the melting-point indicates decomposition, and this latter is increased on further heating : the orange liquid turns dark brown, with considerable evolution of brown fumes. Rapid heating causes explosive decomposition. Nitrogen pentoxide volatilises in dry air, but deliquesces in moist air with the formation of nitric acid.

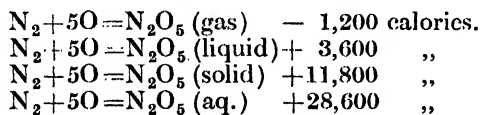
The vapour pressures at various temperatures are as follows :—<sup>4</sup>

Vapour pressure, mm. Hg .	13	32	79	183	420	760
Temperature, ° C. . . . .	–15	–5	+5	+15	+25	+32·5

These values are expressed in the equation

$$\log P = -\frac{1244}{T} + 34\cdot1 \log T - 85\cdot929.$$

The heats of formation are as follows :—



The heat of combination with 1 molecule of water is 2·320 Cals., and with excess of water 16·200 Cals.<sup>3</sup> The calculated heat of evaporation is –4·840 Cals., and heat of fusion –8·280 Cals.<sup>3</sup>

The heats of sublimation in a closed vessel below 30° C. are as follows :—<sup>4</sup>

Temperature, ° C. . . . .	–10	0	+10	+20
Heat of sublimation (cals.) .	12,360	12,760	13,360	14,140

The decomposition <sup>5</sup> of nitrogen pentoxide is a homogeneous reaction, *i.e.* it proceeds in the gas phase and is independent of catalysis or wall effect. The decomposition proceeds according to the equation—

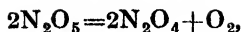
<sup>1</sup> Helbig, *Atti R. Accad. Lincei*, 1903, 12, (i), 211 ; *Zeitsch. Elektrochem.*, 1906, 12, 550.

<sup>2</sup> Russ and Ehrlich, *Zeitsch. Elektrochem.*, 1914, 20, 45.

<sup>3</sup> Berthelot, *Bull. Soc. chim.*, 1874, (ii), 21, 53.

<sup>4</sup> Daniels and Bright, *J. Amer. Chem. Soc.*, 1920, 42, 1131.

<sup>5</sup> White and Tohman, *ibid.*, 1925, 47, 1240 ; Hunt and Daniels, *ibid.*, 1925, 47, 1602.



and is a unimolecular reaction at all temperatures :

$t^\circ$	65	55	45	35	25	0
K	0.292	0.09	0.0299	0.00808	0.00203	0.0000472
Q (cals.)	25,830	22,750	25,370	25,100	24,240	

The "heat of activation," Q, is derived from the Arrhenius equation

$$\frac{d \log K}{dt} = \frac{Q}{RT^2}.$$

It is equal to the quantum of energy required to activate each molecule, multiplied by the Avogadro number N :

$$Q = N h \nu.$$

The reaction constant remains that of a unimolecular reaction down to low pressures :<sup>1</sup>

$p(\text{N}_2\text{O}_5)$	278	281	114	51.6	9.6	0.0264	0.00185
K	0.027	0.027	0.026	0.026	0.027	0.020	0.021

The rate is much the same in inert solvents such as chloroform and carbon tetrachloride.<sup>2</sup>

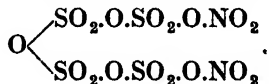
The decomposition of nitrogen pentoxide is retarded by the presence of ozone.<sup>3</sup>

**Chemical Properties.**—Nitrogen pentoxide is a powerful oxidising agent owing to its decomposition with the liberation of oxygen. Many substances when heated in it burn, such as carbon, phosphorus, and sulphur. The latter element gives rise to white vapours which form a sublimate of the composition  $\text{S}_2\text{O}_5(\text{NO}_2)_2$ —nitrosulphonic anhydride.

The pentoxide is a useful nitrating agent for organic compounds, the reaction being similar to that of a mixture of nitric and sulphuric acids.<sup>4</sup>

Nitric acid dissolves nitrogen pentoxide, and a definite compound,  $2\text{HNO}_3 \cdot \text{N}_2\text{O}_5$ , has been obtained which is liquid at ordinary temperatures but solidifies at  $5^\circ \text{C}$ .

Sulphur trioxide reacts with nitrogen pentoxide in carbon-tetrachloride solution, with the formation of a crystalline precipitate melting at  $124^\circ$  to  $128^\circ \text{C}$ ., which is probably  $(\text{SO}_3)_4 \cdot \text{N}_2\text{O}_5$  :<sup>5</sup>



#### NITROSO-NITROGEN TRIOXIDE, $(\text{N}_3\text{O}_4)_x$ .

When nitric oxide is passed through liquid air or oxygen, or when air or oxygen acts on solid nitric oxide at  $-185^\circ \text{C}$ ., a green solid is produced which was assumed to be nitrogen hexoxide,  $\text{NO}_3$  or  $\text{N}_2\text{O}_6$ .<sup>6</sup> The same

<sup>1</sup> Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, 43, 53.

<sup>2</sup> Lueck, *ibid.*, 1922, 44, 757.

<sup>3</sup> Daniels, Wulf, and Karrer, *ibid.*, 1922, 44, 2402. See also Hirst, *Trans. Chem. Soc.*, 1925, 127, 657; Hirst and Rideal, *Proc. Roy. Soc.*, 1925, A109, 526.

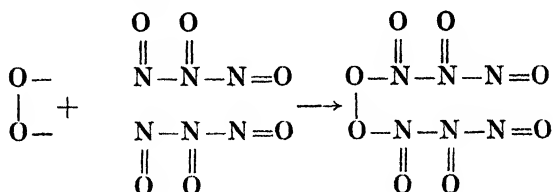
<sup>4</sup> Gibson, *Proc. Roy. Soc. Edin.*, 1908, 28, 705.

<sup>5</sup> Pictet and Karl, *Compt. rend.*, 1907, 145, 238.

<sup>6</sup> Helbig, *Atti R. Accad. Lincei*, 1903, 5, 166; Muller, *Zeitsch. anorg. Chem.*, 1912, 76, 24; 1914, 86, 230.

oxide was considered to be formed by the action of a silent discharge through a mixture of nitrogen, or nitrogen tetroxide and oxygen,<sup>1</sup> or by the action of an induction current on a mixture of nitrogen tetroxide and oxygen.<sup>2</sup>

The green solid mentioned above is now assumed to be nitroso-nitrogen trioxide, having an empirical formula  $N_3O_4$ ,<sup>3</sup> and is produced according to the following reaction:—



This peroxidised polymeride of nitric oxide is irreversibly converted into nitrogen trioxide.

<sup>1</sup> Hautefille and Chappuis, *Compt. rend.*, 1881, 92, 80, 134; 1882, 94, 1111, 1306.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1881, (v), 22, 432.

<sup>3</sup> Hasche, *J. Amer. Chem. Soc.*, 1925, 47, 2143.



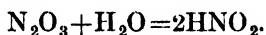
## CHAPTER XI.

### NITROUS ACID.

**History.**—As early as 1777 it was realised that there was more than one “acid of nitre.” Scheele<sup>1</sup> distinguished “phlogisticated acid of nitre” from nitric acid as being a weaker volatile acid produced by the reduction of nitric acid. He also showed that nitre, when strongly heated, lost oxygen, and left a deliquescent salt which readily decomposed into a volatile acid when treated with acid. Priestley<sup>2</sup> had previously described the brown fumes produced by oxidising nitric oxide as “nitrous acid vapour,” while the terms “nitrous acid gas” and “nitrous acid” were used later by Davy and Gay-Lussac respectively. Confusion of terms, however, existed, due to the fact that both nitric and nitrous acids were present, and the means of distinguishing the two were not available at that time. It was understood clearly, however, that there were two distinct salts, nitrates and nitrites, and Cavendish<sup>3</sup> showed that silver nitrite was precipitated when potassium nitrite was added to a solution of silver nitrate. Gay-Lussac<sup>4</sup> was the first to prepare nitric and nitrous acids by the careful oxidation of nitric oxide with oxygen in the presence of water.

Nitrous acid is an unstable compound, and all the methods of preparation yield an aqueous solution of the acid.

**Preparation.**—1. Nitrogen trioxide,  $N_2O_3$ , which is nitrous anhydride, produces a weak solution of nitrous acid when treated with ice-cold water:

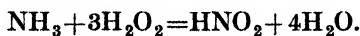


2. Dilute hydrochloric acid decomposes silver nitrite with the liberation of nitrous acid:



3. Alkali nitrites similarly decompose with dilute acids, and this affords a convenient laboratory method. Nitrites may be prepared by reducing nitrates with metals,<sup>5</sup> or sulphites,<sup>6</sup> or electrolytically;<sup>7</sup> also by absorption of nitrogen trioxide by alkalies.<sup>8</sup>

4. Oxidation of ammonia with hydrogen peroxide produces nitrous acid, but there is always some ammonium nitrite present in the solution:<sup>9</sup>



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<sup>1</sup> Scheele, *Treatise on Air and Fire* (1777); *Alcmbic Club Reprints*, VIII, 20.

<sup>2</sup> Priestley, *Experiments on Air*, 1774, I, 110–115.

<sup>3</sup> Cavendish, *Alcmbic Club Reprints*, III, 46.

<sup>4</sup> Gay-Lussac, *Ann. Chim.*, 1816, I, 399.

<sup>5</sup> Fischer, *Pogg. Annalen*, 1848, 74, 115.

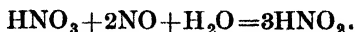
<sup>6</sup> Etard, *Bull. Soc. chim.*, 1877, [2], 27, 434; Le Roy, *Compt. rend.*, 1880, 108, 1251.

<sup>7</sup> Muller and Spitzer, *Zeitsch. Elektrochem.*, 1905, 11, 917.

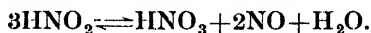
<sup>8</sup> Divers, *Trans. Chem. Soc.*, 1899, 75, 85.

<sup>9</sup> Weith and Weber, *Ber.*, 1874, 7, 1745; Hoppe and Seyler, *ibid.*, 1883, 16, 1916.

5. Nitric oxide passed into nitric acid reduces the latter to nitrous acid :



**Physical Properties of Nitrous Acid.**—The aqueous solution of nitrous acid is blue in colour, which quickly fades with evolution of brown fumes, leaving a solution containing only nitric acid :



The decomposition of nitrous acid is unimolecular, and the strongest solution which can be obtained at 0° C. is 0.185N, prepared from the decomposition of barium nitrite with dilute sulphuric acid.<sup>1</sup>

The aqueous solution is more stable when kept at low temperatures and small concentration, and also when under pressure of nitric oxide. The decomposition of a cold dilute solution follows the reaction



whereas stronger solutions at higher temperatures decompose according to the equations<sup>2</sup>



Other factors also influence the decomposition, such as agitation, surface area, and presence of nitric acid.<sup>3</sup> The decomposition of nitrous acid in dilute acid solutions has been studied.<sup>4</sup>

The heat of formation of nitrous acid is as follows :—<sup>5</sup>

$\text{N}_2\text{O}_3$ , Aq.	= -6,820	calories.
$\text{H}$ , $\text{N}$ , $\text{O}_2$ , Aq.	= 30,770	„
$2\text{NO}$ , $\text{O}$ , Aq.	= 36,330	„
$\text{H}$ , $\text{NO}$ , $\text{O}$ , Aq.	= 52,345	„
$\text{N}_2$ , $2\text{H}_2\text{O}$	= 71,770	„ (product as $\text{NH}_4\text{NO}_2$ )
Heat of solution	= 4,700	„

The decomposition of nitrous acid in dilute solution is attended with the absorption of 18.4 Cals.<sup>6</sup>

The heat of neutralisation with ammonia is 9.100 Cals., and with barium hydroxide 10.600 Cals.<sup>7</sup>

The velocity constant of decomposition is 0.00014 at 0° C., 0.00022 at 21° C., and 0.00057 at 40° C.<sup>1</sup>

The dissociation constant at 0° C. is  $6 \times 10^{-4}$ <sup>1</sup> and the calculated mobility of the  $\text{NO}_2$  ion is 64.5, that determined from  $\text{AgNO}_2$  being 63,<sup>8</sup> and from  $\text{Ba}(\text{NO}_2)_2$  61.7.<sup>9</sup>

The electrical conductivities at 25° C. for dilutions of 512, 1024, and 1536 are 150.7, 189.0, and 217.0 respectively.<sup>10</sup>

<sup>1</sup> Rây, Dey, and Ghosh, *Trans. Chem. Soc.*, 1917, **111**, 413.

<sup>2</sup> Veley, *Proc. Roy. Soc.*, 1893, **52**, 27, 54.

<sup>3</sup> Saposchnikoff, *Chem. Zentr.*, 1908, (ii), 1330. See also Veley, *Trans. Chem. Soc.*, 1917, **111**, 415; Knox and Reid, *J. Soc. Chem. Ind.*, 1919, **28**, 105T; Briner and Durand, *Compt. rend.*, 1912, **155**, 1495.

<sup>4</sup> Klemene and Pollak, *Zeitsch. physikal. Chem.*, 1922, **101**, 150.

<sup>5</sup> Thomsen, *Ber.*, 1879, **12**, 2062.

<sup>6</sup> Briner and Durand, *loc. cit.*

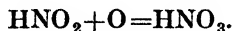
<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1875, (v), **6**, 145.

<sup>8</sup> Pick, *Dissertation*, Breslau, 1906.

<sup>9</sup> Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 385.

<sup>10</sup> Schumann, *Ber.*, 1900, **33**, 527.

**Chemical Properties of Nitrous Acid.**—Nitrous acid functions both as a reducing and an oxidising agent. Thus all the ordinary oxidising agents, such as hydrogen peroxide, permanganates, chromates, ozone, bromine water, are reduced and nitric acid is the product :



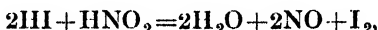
On the other hand, many reducing agents are oxidised, the primary decomposition being :



Stannous chloride is converted into stannic chloride, sulphuretted hydrogen into sulphur, sulphur dioxide into sulphur trioxide. Iodine is liberated from potassium iodide,

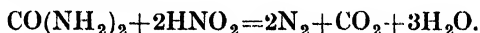


or in acid solution,

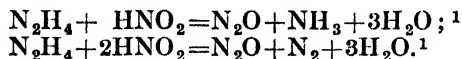


and this reaction is used in the detection of nitrous acid. Many organic colouring matters are bleached by a process of oxidation, *e.g.* indigo, litmus, and methyl orange.

A large number of secondary decomposition products of the reduction of nitrous acid include nitrous oxide, hyponitrous acid, hydroxylamine, nitrogen, and ammonia. Urea and nitrous acid react to give nitrogen and carbon dioxide :



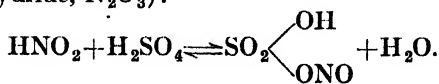
The interaction of hydrazine and nitrous acid seems to be of a complex nature, and the following equations have been given to represent the reactions :—



Azoimide and nitrous acid yield nitrous oxide and nitrogen :<sup>2</sup>



Concentrated sulphuric acid forms nitrosyl-sulphuric acid with nitrous acid (or the anhydride,  $\text{N}_2\text{O}_3$ ):<sup>3</sup>



Sulphurous acid shaken with nitrous acid yields hydroxylamine-disulphonic acid :



(See also p. 108.)

There is no action between nitrites and normal sulphites, but with acid sulphites various salts of hydroxylamine-sulphonic acids are produced.<sup>4</sup>

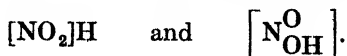
<sup>1</sup> Francke, *Ber.*, 1905, 38, 4102.

<sup>2</sup> Oliveri and Mandala, *Gazzetta*, 1921, 51, i, 138; ii, 201.

<sup>3</sup> Divers and Haga, *Trans. Chem. Soc.*, 1894, 65, 523.

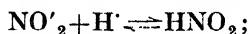
<sup>4</sup> See under Hydroxylamine, p. 107.

**Constitution of Nitrous Acid.**—Nitrous acid resembles nitric acid inasmuch as it shows two kinds of absorption spectra. There is probably an equilibrium between two tautomeric forms:

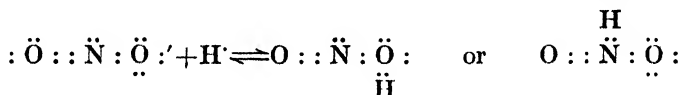


Thus silver nitrite appears to exist in two forms, one an ionisable salt,  $[\text{NO}_2]\text{Ag}$ , and the other a non-electrolyte,  $\left[ \begin{array}{c} \text{N}^{\text{O}} \\ \text{OAg} \end{array} \right]$ . This will account for the fact that the product of the reaction between  $\text{AgNO}_2$  and  $\text{CH}_3\text{I}$  is methyl nitrite,  $\left[ \begin{array}{c} \text{N}^{\text{O}} \\ \text{OCH}_3 \end{array} \right]$ , an ester the hydrolysis of which shows that the methyl group is attached to the oxygen atom; and also of nitro-methane,  $[\text{NO}_2]\text{CH}_3$ , a nitro-paraffin the reduction of which shows that the methyl group is attached to the nitrogen atom.

The modern valency theory represents the tautomerism of nitrous acid and nitrites as due to the shift of the hydrogen atom from oxygen to nitrogen:



or, adopting the theory of the cubic arrangement of octets (see p. 13):



**Detection and Estimation.**—The liberation of iodine from potassium iodide, which gives a blue colour in the presence of starch, is a delicate but not characteristic test for nitrous acid or nitrites in acid solution.

Metaphenylene diamine in hydrochloric acid produces a brown colour. A very sensitive reagent is an acetic-acid solution of sulphanilic acid and  $\beta$ -naphthylamine (Griess-Ilosvay reagent), which gives a pink colour with nitrites, sensitive to 1 part per million of water.

1. The estimation of nitrites and nitrous acid may be carried out by direct titration with standard potassium permanganate. The solution is run from a burette into a standard solution of permanganate until the colour is just discharged.

A modification of this method <sup>1</sup> is to add a known excess of standard permanganate solution to the nitrite, acidify with sulphuric acid, liberate iodine by adding potassium iodide, and titrate with sodium thiosulphate, which gives the unused permanganate.

2. The liberation of iodine from potassium iodide by nitrites may be used directly, and the iodine estimated with thiosulphate. The solution should be allowed to stand for two minutes before titration with the thiosulphate, otherwise high results are obtained.

3. A nitrometer method <sup>2</sup> of estimation may be used where presence of organic acids rules out the permanganate method. The nitric oxide evolved is directly measured, but the reaction requires the presence of potassium ferrocyanide, and also of one organic acid such as acetic, tartaric, citric, or oxalic:



<sup>1</sup> Raschig, *Ber.*, 1905, 38, 3911.    <sup>2</sup> Maderna and Coffetti, *Gazzetta*, 1907, 37, (i), 595

Two factors likely to cause errors in this method are the solubility of the nitric oxide in the aqueous solution, and the vapour pressure of the acetic acid.

4. Among other methods which have been proposed is the decomposition of nitrites by hydrazine sulphate and measuring the volume of nitrogen, two-thirds of which is due to nitrite;<sup>1</sup> also the reaction with hydroxylamine hydrochloride and titration with sodium hydroxide before and after the reaction.<sup>2</sup>

The reaction with azoimide, yielding nitrogen and nitrous oxide, is also quantitative in dilute solution, and is used in the estimation of nitrites.<sup>3</sup> Nitrites may be determined gravimetrically by a reaction with an excess of silver bromate and acetic acid. The nitrous acid forms an equivalent amount of silver bromide by reduction.<sup>4</sup>

<sup>1</sup> Dey and Sen, *Zeitsch. anorg. Chem.*, 1911, **171**, 236.

<sup>2</sup> Sanin, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 791.

<sup>3</sup> Sommer and Pincas, *Ber.*, 1915, **48**, 1833, 1963.

<sup>4</sup> Busvold, *Chem. Zcit.*, 1914, **38**, 5 ; 1915, **39**, 215.

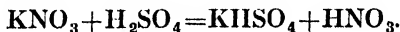
## CHAPTER XII.

### NITRIC ACID.

**History.**—Nitric acid was one of the earliest nitrogen compounds to be used, as it was known to the Egyptians. Its preparation was first described by Geber in A.D. 778, who obtained it by distilling a mixture of nitre, blue vitriol, and alum. In the thirteenth century Lullius prepared it from nitre and iron sulphate, while Glauber in 1648 showed its production from nitre and oil of vitriol. Known under such names as “aqua-fortis,” “spiritus nitri acidus,” and “spiritus nitri fumans Glauberi,” it was largely used by the alchemists for the separation of silver and gold. Mayow in 1669 was the first to propound a theory as to its composition, as he recognised that the same substance was present in nitre as in the air which supported combustion, namely, dephlogisticated air (oxygen). In 1776 Lavoisier<sup>1</sup> showed that oxygen was a definite constituent of nitric acid, although he was unable to show how it was combined with the other constituents. Cavendish<sup>2</sup> in 1784 showed that nitric acid was produced by passing electric sparks through a mixture of nitrogen and oxygen, and about the same time it was proved by Lavoisier and Priestley that it consisted only of nitrogen, oxygen, and water.

**Occurrence.**—Free nitric acid is only found in nature in small amounts, chiefly in rain-water, where it has been produced by electrical discharges in the atmosphere. Neutralisation of rain-water occurs by means of soil bases with the formation of nitrates, and this salt production is also the result of free nitric-acid formation by the oxidation of nitrogenous organic matter.<sup>3</sup>

**Preparation.**—1. The laboratory method for preparing nitric acid is to distil dry potassium nitrate with an equal weight of concentrated sulphuric acid in a retort, and to collect the nitric acid in a well-cooled flask :



The distillation is carried out at as low a temperature as possible, and the product is of a distinctly yellow colour owing to the presence of nitrogen peroxide. Purification may be effected by redistilling with an equal volume of concentrated sulphuric acid, and blowing a current of air through this distillate, which has been gently warmed.

2. Combination of nitrogen and oxygen by passing through the electric arc, and absorbing the oxides of nitrogen in water.<sup>4</sup>

3. Oxidation of ammonia by means of a catalyst.<sup>5</sup>

<sup>1</sup> Lavoisier, *Œuvres*, ii, 226.

<sup>2</sup> Cavendish, *Phil. Trans.*, 1784, 110; 1785, 372.

<sup>3</sup> See p. 23.

<sup>4</sup> See Fixation of Nitrogen—Arc process.

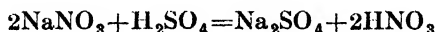
<sup>5</sup> See Fixation of Nitrogen—Oxidation of ammonia.

Nitric acid is obtained by a number of other reactions which can scarcely be called methods of preparation :

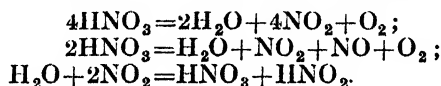
- (a) Burning hydrogen in air.
- (b) Passing electric sparks through moist air.
- (c) Action of silent electric discharge on a mixture of nitrogen and oxygen in the presence of water.

#### MANUFACTURE OF NITRIC ACID FROM SODIUM NITRATE.

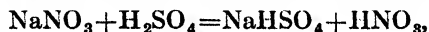
The decomposition of sodium nitrate (Chili saltpetre) still remains one of the most important processes for the manufacture of nitric acid. The complete reaction shown by the equation



is not carried out in practice for a number of reasons. The high temperature necessary for the reaction ( $900^\circ \text{C.}$ ) involves high fuel consumption, excessive wear and tear of plant, and decomposition of nitric acid, which causes the product to be dilute, and to contain a high percentage of nitrous acid, according to the following reactions :—



Further, it would not be possible to remove the residual sodium sulphate at all readily from the retort owing to its high melting-point ( $860^\circ \text{C.}$ ). In consequence, nearly double the quantity of sulphuric acid is used,



as the reaction represented by the above equation proceeds at a relatively low temperature ( $200^\circ \text{C.}$ ), and the residual sodium bisulphate (nitre cake) can be run off from the retort.

The plant consists of a retort, condenser, receiver, and absorbing system for the oxides of nitrogen.

**Retort.**—This is a large cast-iron cylindrical vessel. As a typical example the Waltham retort may be mentioned, which has a cubical capacity of about 350 cubic feet, is 8 feet 6 inches by 6 feet 9 inches, and takes a charge of two tons of sodium nitrate. The quantity and concentration of sulphuric acid depend upon the dryness of the nitrate, the proportions being approximately 85 of nitrate to 80 of acid. The retort is surrounded by brickwork 18 inches thick, and is fired by coal, coke, oil, or gas. Whatever fuel is used, the flues are so arranged that the hot gases circulate round the retort so as to produce even heating.

**Condensing System.**—The vapours from the retort are conducted through a silicon iron or fused silica pipe to the condensers. The conduit pipe is made of as simple form as possible in order to provide an easy flow. Various forms of condensers are in use at the present time, and some characteristics of these will be given.

**Guthmann Condenser.**—This condenser consists of perpendicular pipes cooled in water, and was in extensive use at one time. Owing to high working costs and general inflexibility of the plant, however, this system is not used much in modern practice.

**Hart Condenser.**—The outstanding feature of this system is the

employment of glass tubes fitted between standards of pottery or silicon iron. The tubes, 6 feet long and  $1\frac{1}{2}$  inches (English) or 3 inches (American) diameter, are slightly inclined to the horizontal, and are cooled by water trickling over the outside. Excellent condensation is effected and the progress of distillation can be watched; further, broken tubes can be replaced without interrupting the operation. On the other hand, the system is of an intricate nature, and its maintenance is expensive owing to the large number of joints.

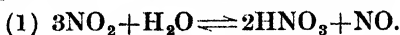
*Valentiner Condenser.*—This system differs from all others inasmuch as it works under reduced pressure. The chief condensation takes place in coils totally immersed in water, but some condensation also occurs in air-cooled Woulff's bottles, which act as receivers. All joints have to be carefully watched owing to the reduced pressure of the distillation, consequently high labour costs are involved.

*Hough Condenser.*—Condensation of the hot vapours is effected by passing through a series of double U-tubes contained in a rectangular box and cooled by water. Acid-resisting iron is used, and this condenser is both compact and efficient.

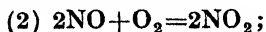
*S-pipe Condenser.*—Modern practice favours a relatively simple type of air-cooled condenser in the form of a series of S-bends. Fused silica ware or silicon iron is used, and one advantage seems that such a type requires but little attention.

**Receivers.**—These vessels are made of various materials—depending on the strength of acid to be collected and other conditions—but earthenware seems to be the only really safe material. Fume-tight lids have to be fitted, and of course provision has to be made for conveying fumes into the absorption system.

**Absorbers.**—An efficient absorbing system is imperatively required, as often as much as 10 per cent. of the original nitrogen content of the sodium nitrate passes through the condensers as nitrogen peroxide,  $\text{NO}_2$ . Nitric oxide,  $\text{NO}$ , nitrosyl chloride,  $\text{NOCl}$ , chlorine, nitric acid vapour and water-vapour are also present. Absorption of nitrogen peroxide in water proceeds according to the equation



This nitric oxide, together with that produced during the distillation, has to be oxidised to the peroxide again :



which means that an adequate air supply must be introduced into the absorbing systems. Two further points of great importance are the retarding of the absorption of nitrogen peroxide by the presence of nitric oxide (equation (1) is reversible), and also the fact that reaction (2) requires appreciable time for completion.

The fume main from the condensers and receivers enters at the bottom of one of a series of towers, and the nitrous gases are pumped to the top, meeting a stream of water. The tower is filled with quartz packing, so as to provide as large a surface as possible for absorption by the water. The dilute nitric acid thus produced is pumped to the top of the next tower, while the gases are led in at the bottom, and the absorption and oxidation are repeated. The strongest acid obtainable is 60 per cent., and when this concentration is reached, the acid is drawn off and the absorption cycle continued with fresh water.



**Concentration.**—The strength of the nitric acid collected in the receivers depends upon the dryness of the sodium nitrate and the concentration of the sulphuric acid. It is possible to obtain nitric acid of an average strength of 90 per cent. by using dry nitrate and sulphuric acid of 90 to 94 per cent. concentration. The total yield of nitric acid is smaller, however, as the nitre cake retains some of the nitrogen compounds, and the resulting acid has a high nitrous acid content. A greater amount of nitric acid of average strength of 80 per cent. is obtained by using wet nitrate (2 to 2.5 per cent. water content) and Glover sulphuric acid (78 per cent.  $\text{H}_2\text{SO}_4$  content). Nitric acid of 99.6 per cent. concentration is obtained by distilling weaker acid with concentrated sulphuric acid. The retort, such as is used in the manufacture, can be used as a still, and condensing and absorbing systems similar to those described above are used in conjunction with the distillation, which is carried out at about  $135^\circ \text{C}$ . Acids ranging in concentrations from 100 per cent. downwards may be obtained by running off from the receivers at various stages.

A process of "bleaching" is generally employed to remove nitrous acid in the form of oxides of nitrogen from the commercial acid. Generally this is brought about by blowing a stream of hot air through the acid, although in some plants the bleaching process is incorporated with the condensing operation, so that the distillate encounters the hot retort gases on the counter-current principle, with the result that not more than 1 per cent. of nitrous acid remains.

Commercial nitric acid contains as impurities hydrochloric acid, sulphuric acid, iodine, iron salts, and nitrogen peroxide. The hydrochloric acid is derived from the chlorides present in the nitrate (0.5 per cent.), and a certain amount is oxidised to chlorine by the nitric acid, as well as to nitrosyl chloride,  $\text{NOCl}$ . Traces of sulphuric acid are carried over from the retort, and the iodate in the nitrate is responsible for the small amounts of iodine. The iron salts, of course, are derived from the apparatus.

**Physical Properties of Nitric Acid.**—Pure nitric acid only exists at  $-41^\circ \text{C}$ . in the form of snow-white crystals, which decompose slightly on liquefying, into nitrogen pentoxide,  $\text{N}_2\text{O}_5$ , and water. Passing a current of dry air through this liquid removes the  $\text{N}_2\text{O}_5$ , and leaves a colourless liquid with a 98.67 per cent. content of nitric acid.<sup>1</sup>

Distillation of concentrated nitric acid with concentrated sulphuric acid in an atmosphere of carbon dioxide gives a product containing 98 to 99 per cent.  $\text{HNO}_3$ . Nitric acid containing 99.8 per cent.  $\text{HNO}_3$  is slightly yellow, with a pungent smell, and fumes strongly in air.<sup>2</sup>

A study of the freezing-point curves (see fig. 20) shows two maxima, and Pickering<sup>3</sup> isolated two crystalline hydrates corresponding to  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  at  $-18^\circ \text{C}$ ., and  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  at  $-36.8^\circ \text{C}$ . Küster and Kremann<sup>4</sup> give these two maxima as  $-18.5^\circ \text{C}$ . and  $-38^\circ \text{C}$ .

Roscoe<sup>5</sup> gave the boiling-point of the purest liquid nitric acid under atmospheric pressure as  $86^\circ \text{C}$ ., but slight decomposition begins below this temperature.

<sup>1</sup> Küster and Münch, *Zeitsch. anorg. Chem.*, 1905, **43**, 350–355.

<sup>2</sup> Aston and Ramsay, *Trans. Chem. Soc.*, 1894, **65**, 169.

<sup>3</sup> Pickering, *ibid.*, 1893, **63**, 436. Also see p. 196.

<sup>4</sup> Kremann, *Zeitsch. anorg. Chem.*, 1904, **41**, 22.

<sup>5</sup> Roscoe, *Trans. Chem. Soc.*, 1861, **13**, 146.

Creighton and Githens<sup>1</sup> have determined the boiling-points of nitric acid of 99.79 per cent. purity under different pressures, which are given in the following table :—

Pressure, mm. Hg.	Boiling-point, ° C.	Pressure, mm. Hg.	Boiling-point, ° C.
47	22.1	290	57.1
51	24.5	346	62.1
60	26.2	360	63.4
90	31.7	425	68.5
110	35.6	500	72.7
125	38.5	580	77.2
203	49.0	675	82.5
250	53.5		

An aqueous solution of constant boiling-point (120.5° C.) is obtained when any solution of nitric acid is distilled. A concentrated solution will give a distillate of decreasing nitric acid content until, under atmospheric pressure, the residue has a concentration of 68 per cent. Similarly, a dilute solution will eventually reach the same concentration, when it will boil unchanged. The density of this constant boiling solution is 1.414 at 15.5° C., and Roscoe found that the composition varied with pressure, which indicates that this constant boiling solution is not a definite hydrate of nitric acid.<sup>2</sup>

The vapour pressures of solutions of nitric acid of different concentrations and at different temperatures have been determined by Creighton and Githens<sup>1</sup> and Saposchnikoff.<sup>3</sup> Reference has already been made to the necessity of keeping the temperature as low as possible during the preparation of nitric acid from sodium nitrate and sulphuric acid. The thermal decomposition of nitric acid is shown in the following table :—<sup>4</sup>

Temperature, ° C.	Percentage Decomposition.	Temperature, ° C.	Percentage Decomposition.
86	9.53	190	49.34
100	11.77	220	72.07
130	18.79	250	93.03
160	28.96	256	100.00

The following table<sup>5</sup> shows the variation of density with concentration of aqueous solutions of nitric acid :—

<sup>1</sup> Creighton and Githens, *J. Franklin Inst.*, 1915, 179, 161.

<sup>2</sup> Roscoe, *Trans. Chem. Soc.*, 1861, 13, 146.

<sup>3</sup> Saposchnikoff, *Zeitsch. physikal. Chem.*, 1905, 53, 225.

<sup>4</sup> Carius, *Ber.*, 1871, 4, 828.

<sup>5</sup> Lunge and Rey, *Zeitsch. angew. Chem.*, 1891, 4, 165.

## DENSITIES AND PERCENTAGES OF NITRIC ACID.

Density.	Percentage HNO <sub>3</sub> .	Density.	Percentage HNO <sub>3</sub> .	Density.	Percentage HNO <sub>3</sub> .
1.000	0.10	1.100	17.11	1.300	47.49
1.005	1.00	1.120	20.23	1.350	55.79
1.010	1.90	1.140	23.31	1.400	65.30
1.020	3.70	1.160	26.36	1.450	77.28
1.030	5.50	1.180	29.38	1.475	84.45
1.040	7.26	1.200	32.36	1.500	94.09
1.060	10.68	1.250	39.82	1.520	99.67
1.080	13.95				

The effect of dissolving nitrogen peroxide in nitric acid is to raise the density, and the table below <sup>1</sup> gives the increase in density of nitric acid,  $D_4^{15}=1.4960$ .

INFLUENCE OF NITROGEN PEROXIDE ON  
NITRIC ACID.

( $D=1.4960$ .)

Percentage N <sub>2</sub> O <sub>4</sub> .	HNO <sub>3</sub> Increase in Density.	Percentage N <sub>2</sub> O <sub>4</sub> .	HNO <sub>3</sub> Increase in Density.
0.5	0.00075	6.0	0.03950
1.0	0.00300	7.0	0.04650
2.0	0.01050	8.0	0.05325
3.0	0.01800	10.0	0.06600
4.0	0.02525	12.0	0.07850
5.0	0.03225		

The average increase in density per cent. from 1 to 5 per cent. of nitrogen peroxide is 0.00585, and from 5 to 12 per cent. is 0.00660.

The average increase in density from 1 to 5 per cent. of nitrogen peroxide on nitric acid  $D_4^{15}=1.5126$ <sup>2</sup> and  $D_4^{15}=1.5130$ <sup>3</sup> is 0.0035 per 1 per cent. nitrogen peroxide, and from 5 to 20 per cent. of nitrogen peroxide is 0.0040 per 1 per cent. nitrogen peroxide.

Pascal and Garnier<sup>2</sup> found that the maximum weight of nitrogen peroxide dissolved was 42.5 per cent., which corresponds to a hydrate of the formula  $N_2O_5 \cdot N_2O_4 \cdot H_2O$ , which was stable below  $-48.5^\circ \text{C}$ .

Contraction in volume occurs when nitric acid and water are mixed,

<sup>1</sup> Lunge and Marchlewski, *Zeitsch. angew. Chem.*, 1892, 5, 10, 330.

<sup>2</sup> Pascal and Garnier, *Bull. Soc. chim.*, 1919, 25, 309.

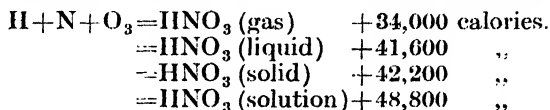
<sup>3</sup> Bonsfield, *Trans. Chem. Soc.*, 1919, 115, 48.

and the maximum contraction occurs corresponding to the ratio  $2\text{HNO}_3 : 3\text{H}_2\text{O}$ .<sup>1</sup>

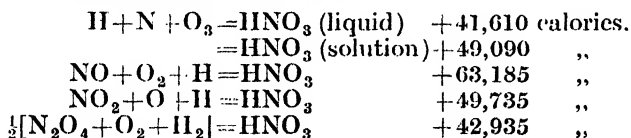
The following table <sup>2</sup> gives the contractions for various concentrations of nitric acid :—

Percentage $\text{HNO}_3$ .	Temperature, ° C.	Contraction.	Percentage $\text{HNO}_3$ .	Temperature, ° C.	Contraction.
19·37	14·2	0·03685	65·80	14·2	0·06104
25·50	„	0·04650	78·22	„	0·04528
30·17	24·2	0·05171	87·90	„	0·02500
33·87	„	0·05571	92·34	„	0·01626
42·40	14·2	0·06690	95·62	„	0·00672
52·80	„	0·07040	99·97	„	0·00008
60·60	„	0·06592			

The heats of formation have been determined by Berthelot : <sup>3</sup>



The values obtained by Thomsen <sup>4</sup> are :



The molecular heat of fusion = 601 calories.<sup>5</sup>

The molecular heat of evaporation = 7250 „

The following table gives the values of the heat of solution in Cals. as determined by Thomsen <sup>6</sup> and Berthelot,<sup>7</sup> when 1 gram molecule of nitric acid is dissolved in  $n$  gram molecules of water :—

No. of molecules of $\text{H}_2\text{O}$ . . .	0·5	1	1·5	2	2·5	3	4	5	6
Thomsen, 18° C.	2·00	3·29	4·16	..	5·27	5·71	..	6·66	..
Berthelot, 10° C.	2·03	3·34	4·16	4·86	..	5·76	6·39	6·76	6·98
No. of molecules of $\text{H}_2\text{O}$ . . .	8	10	20	40	80	100	160	200	320
Thomsen, 18° C.	..	7·32	7·46	7·44	7·42	7·44	7·45	..	7·49
Berthelot, 10° C.	7·22	7·27	7·36	7·27	..	7·21	..	7·18	

<sup>1</sup> Kolb, *Ann. Chim. Phys.*, (iv), 10, 136.

<sup>2</sup> Velej and Manley, *Proc. Roy. Soc.*, 1902, 69, 86–119; *Trans. Chem. Soc.*, 1903, 83, 1015–1021.

<sup>3</sup> Berthelot, *Compt. rend.*, 1880, 90, 779.

<sup>4</sup> Thomsen, *Ber.*, 1879, 12, 2062.

<sup>5</sup> Berthelot, *Ann. Chim. Phys.*, 1877, (v), 12, 530.

<sup>6</sup> Thomsen, *Thermochemische Untersuchungen*, Leipzig, 1883, Band 3.

<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1885, 5, 4, 468.

It will be seen that the maximum heat of dilution occurs when the ratio of nitric acid to water is 1 : 20, so that further dilution will not cause temperature change.

The heat of neutralisation of nitric acid with potassium hydroxide is 13·770 Cals., and with sodium hydroxide 13·680 Cals.<sup>1</sup>

The refractive indices of nitric acid of different concentrations have been studied by Veley and Manley,<sup>2</sup> and the following table shows the values of  $n$  for sodium light at 14·2° C. :—

Percentage HNO <sub>3</sub> .	$n_D$ .	Percentage HNO <sub>3</sub> .	$n_D$ .
2·19	1·336208	70·04	1·406094
6·76	1·342298	78·07	1·405091
18·27	1·358541	87·20	1·402412
32·60	1·377798	95·60	1·398148
41·45	1·388788	98·67	1·396980
50·00	1·398435	99·87	1·397167

The values for the refractive index increase up to about 70 per cent. concentration, and then decrease gradually to 98·67 per cent., and then again increase slightly. The value of  $n$  for the anhydrous acid is practically the same as that for the 50 per cent. acid.

The viscosities,  $\eta$ , of nitric-acid solutions as determined by Küster and Kremann<sup>3</sup> at 15° C. and -15° C. show that the values reach a maximum in each case where the concentration is 65 per cent. The viscosity of water at 0° C. is taken as unity.

Percentage HNO <sub>3</sub>	98·5	82·0	70·0	65·0	50·0	30·0	10·0
$\eta$ at +15° C.	0·548	1·036	1·277	1·300	1·144	0·822	0·655
$\eta$ at -15° C.	0·833	2·240	3·268	3·304	2·369	1·635	..

The magnetic rotatory power of nitric acid is given in the following table,<sup>4</sup> and a gradual decrease in the value of the molecular rotation occurs, corresponding with increase in dilution : —

Molecular Composition.	Percentage HNO <sub>3</sub> .	Specific Rotation at 15° C.	Molecular Rotation.	Molecular Rotation less that due to H <sub>2</sub> O.
HNO <sub>3</sub> + 0·019H <sub>2</sub> O	99·45	0·5292	1·226	1·207
+ 2·701H <sub>2</sub> O	56·44	0·8042	3·678	0·977
+ 7·311H <sub>2</sub> O	32·86	0·9066	8·163	0·852
+ 9·555H <sub>2</sub> O	26·81	0·9238	10·360	0·805
+ 12·080H <sub>2</sub> O	22·54	0·9350	12·788	0·753

<sup>1</sup> Thomsen, *Thermochemische Untersuchungen*, 1906, p. 40.

<sup>2</sup> Veley and Manley, *Proc. Roy. Soc.*, 1902, 69, 114.

<sup>3</sup> Küster and Kremann, *Zeitsch. anorg. Chem.*, 1904, 41, 13.

<sup>4</sup> W. H. Perkin, senior, *Trans. Chem. Soc.*, 1893, 63, 65.

The following values of molar conductivity  $\lambda$ , in which the dilutions  $V$  are in litres per molecule, were determined at  $18^\circ \text{C.}$  : -<sup>1</sup>

$V = 0.1$	0.2	0.5	1.0	2.0	5.0	10.0
$\lambda = 65.4$	156	258	310	324	340	350
$V = 20$	50	100	200	500	1000	
$\lambda = 357$	364	368	371	374	375	

The temperature coefficient of conductivity,  $\frac{1}{x_{18}} \cdot \frac{x_{26} - x_{18}}{8} = 0.0162$ ,<sup>1</sup> varies with the dilution.<sup>2</sup>

The mean coefficient per  $1^\circ$  between  $18^\circ$  and  $52^\circ \text{C.}$  is :

	0.0157	0.0154	0.0152	0.0147	0.0143
At $V = \infty$		1000	100	10	$2^3$

The values of the molar conductivities  $\lambda$  have been obtained up to  $100^\circ \text{C.}$ <sup>4</sup>

$t^\circ \text{C.}$	( $V = 1$ ), mols./litre.	0.05, mols./litre.	0.01, mols./litre.	0.002 mols./litre	0.0001 mols./litre.
18	$\lambda = 346.4$	353.7	365.0	371.2	377
25	$\lambda = 385.0$	393.3	406.0	413.7	421
100	$\lambda = 728.0$	760.0	786.0	806.0	826

The conductivities of acids from 20 to 89.4 per cent. have also been determined<sup>5</sup> at  $-16^\circ \text{C.}$

### Freezing-points and Compositions of the System $\text{HNO}_3\text{-H}_2\text{O}$ : <sup>6</sup>

Mols. per cent.

$\text{HNO}_3$	0.0	4.5	9.5	12.2	15.8	19.8	25.0	33.3	37.7
Temp., $^\circ \text{C.}$	0.0	-10.3	-27.1	-43.0*	-30.6	22.9	18.5*	-26.6	-35.4

Mols. per cent.

$\text{HNO}_3$	40.6	44.4	48.9	50.3	61.3	67.1	73.2	80.0	100.0
Temp., $^\circ \text{C.}$	-42.0*	-39.4	-37.9*	-38.2*	-44.4	-55.3	64.5	-55.3	-41.2*

The values marked \* are fixed temperatures or halt-points of crystallisation, *i.e.* either eutectics or melting-points of compounds. As in the case of other strong mineral acids, the freezing-point composition curve (fig. 21) shows the existence of a series of hydrates and eutectics. The hydrates<sup>6</sup> are  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  (melting-point  $-18.5^\circ \text{C.}$ ) and  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  (melting-point  $-38^\circ \text{C.}$ ). The freezing-point curve also shows three eutectics as minima between the four separate components, these eutectics corresponding to the cryohydrates  $\text{ice} + \text{HNO}_3 \cdot 3\text{H}_2\text{O}$  (melting-point  $-43^\circ \text{C.}$ ),  $\text{HNO}_3 \cdot 3\text{H}_2\text{O} + \text{HNO}_3 \cdot \text{H}_2\text{O}$  (melting-point  $-42^\circ \text{C.}$ ), and  $\text{HNO}_3 \cdot \text{H}_2\text{O} + \text{HNO}_3$  (melting-point  $-66^\circ \text{C.}$ ).

<sup>1</sup> Kohlrausch and Grotian, *Wied. Annalen*, 1885, 26, 161.

<sup>2</sup> Déguisne, *Dissertation*, Strassburg, 1895.

<sup>3</sup> Arrhenius, *Zeitsch. physikal. Chem.*, 1889, 4, 96.

<sup>4</sup> Noyes, Melcher, and Cooper, *Zeitsch. physikal. Chem.*, 1910, 70, 358.

<sup>5</sup> Küster and Kremann, *Zeitsch. anorg. Chem.*, 1904, 41, 1.

<sup>6</sup> See also Pickering, *Trans. Chem. Soc.*, 1893, 63, 436.

**Freezing-points and Dissociation in Dilute Solutions.**—Nitric acid ranks with hydrochloric acid as being one of the strongest acids. This is due to the high concentration of hydrogen ions in dilute solution resulting from the far-reaching dissociation of nitric acid in water. The degree of dissociation calculated from the depression of the freezing-point of water is shown in the following table :—<sup>1</sup>

HNO <sub>3</sub> in mols. per litre	0.001054	0.003158	0.007378	0.01153	0.05103	0.1059
Depression of F.P. ( $\Delta t$ )	0.0040	0.0119	0.0276	0.0430	0.1890	0.3735
van 't Hoff factor ( $i$ )	2.008	1.994	1.979	1.973	1.958	1.866
Degree of dissociation ( $\alpha$ )	100.8	99.4	97.9	97.3	95.8	86.6

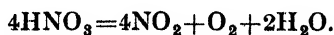
The depression of the freezing-points of more concentrated solutions of nitric acid are given below :<sup>2</sup>

HNO <sub>3</sub> in mols. per litre	0.25	0.5	1.0	1.5	2.0	2.5	3.0
Depression of F.P. ( $\Delta t$ )	0.875	1.810	3.796	5.938	8.347	11.046	13.909

### THE SPECIFIC HEATS OF NITRIC ACID OF VARIOUS CONCENTRATIONS.<sup>3</sup>

Percentage HNO <sub>3</sub> .	Mean Specific Heat.	Temperature of Determination.	Authority.
1.72 (200 mols. H <sub>2</sub> O)	0.982	18° C.	Thomsen, <i>Thermochemisches Untersuchungen</i> , 1906, p. 40.
3.40 (100 " )	0.963		
15.00 (20 " )	0.849		
26.00 (10 " )	0.768		
10.00	0.900	20° C.	Pascal and Garnier, <i>Bull. Soc. chim.</i> , 1920, (iv), 27, 8.
25.57	0.787		
40.00	0.669		
60.52	0.637		
81.80	0.575		
92.15	0.500		
98.15	0.475		

**Chemical Properties of Nitric Acid.**—The outstanding property of nitric acid is its oxidising nature. Its corrosive action on the skin produces painful wounds, and even dilute nitric acid causes an intense yellow coloration due to the formation of xantho-proteic acids. Hair, wool, silk, and many other organic substances are coloured similarly. The decomposition of nitric acid by heat is readily shown by supporting a churchwarden clay pipe so that the stem is inclined downwards with the end under a beehive shelf in a trough of water. An inch or two of the stem is raised to a red heat by a burner, and a few cubic centimetres of nitric acid poured into the bowl. Decomposition occurs according to the equation



<sup>1</sup> Jones, *Zeitsch. physikal. Chem.*, 1893, 12, 630.

<sup>2</sup> Jones and Getman, *Amer. Chem. J.*, 1902, 27, 433.

<sup>3</sup> See also Marignac, *Annalen*, 1872, 8, 335.

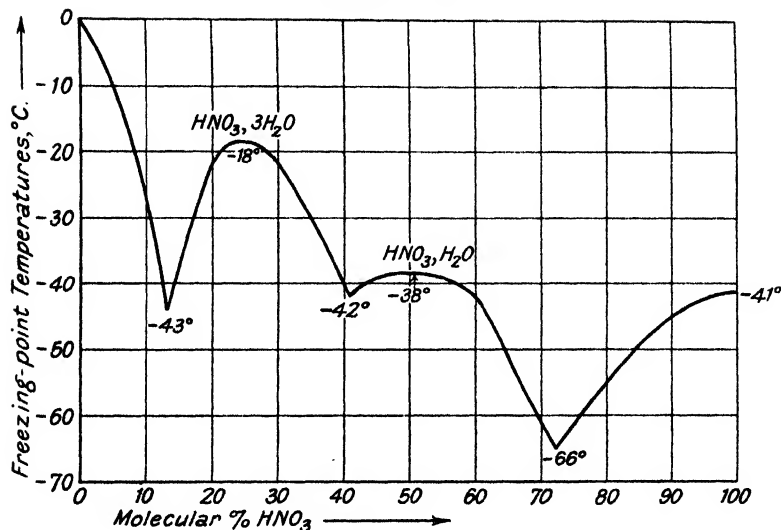


FIG. 21.—Freezing-point curve of aqueous nitric acid.

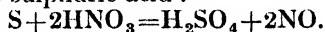
The oxygen can be collected in a gas cylinder over water, while the nitrogen peroxide dissolves with the formation of nitric and nitrous acids.

A large number of products result from the reduction of nitric acid, and the following can be identified under different conditions : nitrous acid  $\text{HNO}_2$ , nitrogen peroxide  $\text{NO}_2$ , nitric oxide  $\text{NO}$ , nitrous oxide  $\text{N}_2\text{O}$ , nitrogen  $\text{N}_2$ , ammonia  $\text{NH}_3$ , and hydroxylamine  $\text{NH}_2\text{OH}$ .

*Action of Nitric Acid on Non-Metals.*—Most non-metals are quickly oxidised in many cases to their highest state of oxidation, and often this occurs violently. Thus phosphorus is converted first into phosphorous and then into phosphoric acid :



Sulphur is oxidised to sulphuric acid :



Iodine is oxidised to iodic acid :



Boron is converted into boric acid and selenium into selenious acid.

*Action of Nitric Acids on Compounds.*—Sulphuretted hydrogen is oxidised to sulphur, sulphur dioxide to sulphuric acid, with production of nitric oxide. In the presence of concentrated sulphuric acid, nitrosyl-sulphuric acid is produced.<sup>1</sup>

Hydrogen bromide yields bromine and nitrogen peroxide, while hydrogen iodide gives iodine and nitric oxide. Hydrogen chloride produces a solution which contains nitrosyl chloride and chlorine (aqua-regia = 4 vols. conc.  $\text{HCl}$  + 1 vol. conc.  $\text{HNO}_3$ ) :



<sup>1</sup> Weber, *Pogg. Annalen*, 1861, 341.

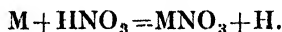


Ferrous salts are oxidised to ferric with production of nitric oxide; stannous salts give stannic salts, hydroxylamine, and ammonia. Arsenious chloride and arsenious oxide give arsenic acid, and similarly antimony chloride is oxidised to antimonious acid.

**Action of Nitric Acid on Metals.** - Nitric acid has no action on gold, platinum, iridium, tantalum, rhodium, and titanium.<sup>1</sup> All other metals are attacked by the acid, often with the formation of nitrates, and reduction products of the nitric acid, which vary with the temperature and concentration of the acid.

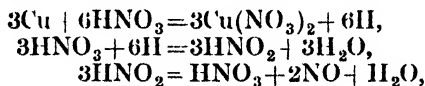
Pelouze and Frémy<sup>2</sup> described the reactions of copper and silver with nitric acid, and showed that tin differed from these in the production of ammonia.

The mechanism of the reaction between nitric acid and various metals has been the subject of considerable controversy for many years. Armstrong and Ackworth<sup>3</sup> put forward the theory that nascent hydrogen was the initial substance which brought about reduction of nitric acid:

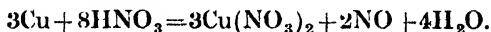


This nascent hydrogen did not escape from the solution owing to the powerful oxidising nature of nitric acid, but produced as secondary products nitrous acid, hyponitrous acid, hydroxylamine, and ammonia. Tertiary reactions occurred from the decomposition of these secondary products, with the formation of nitric oxide, nitrogen trioxide, and nitrous oxide; while double decomposition between the secondary products resulted in the formation of nitrogen and nitrous oxide.

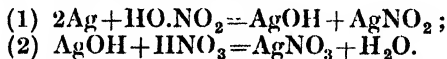
Thus the action of dilute nitric acid on copper, silver, mercury, and bismuth was similar, as shown by the equations



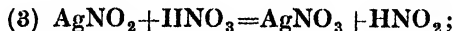
which gives, on summing up,



Divers<sup>4</sup> considered that metals may be divided into two classes with reference to their action on nitric acid. In the first class are placed the four metals copper, silver, mercury, and bismuth, and the primary products are nitrite, nitrate, and water:



Further action of the nitric acid on the nitrite produces nitrous acid and nitrate:



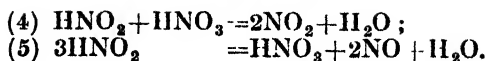
while the nitrous acid reacts to produce nitrogen peroxide or nitric oxide according as the nitric acid is concentrated or dilute, as shown in the following equations:—

<sup>1</sup> Gmelin, *Handbook of Chemistry* (English translation), 1849, Vol. ii., p. 363.

<sup>2</sup> Pelouze and Frémy, *Traité de Chimie*, 1860, i, 351.

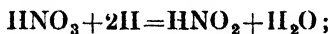
<sup>3</sup> Armstrong and Ackworth, *Trans. Chem. Soc.*, 1877, 15, 54.

<sup>4</sup> Divers, *ibid.*, 1883, 43, 443; 1885, 47, 231.

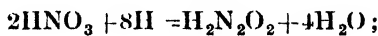


Divers assumed that a very small quantity of nitrous acid is necessary to initiate the reaction and functions in a catalytic manner. There is no formation of ammonia or hydroxylamine at any stage of the reaction.

The second class of metals includes zinc, magnesium, aluminium, cadmium, tin, lead, iron, and the alkali metals, and no nitrous acid is required to start their reaction with nitric acid. According to Divers, nitrous acid is not produced in appreciable amounts, because further reduction occurs which is due to the action of nascent hydrogen :



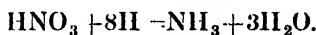
Nitrous  
acid.



Hyponitrous  
acid.

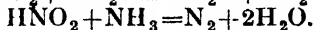
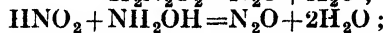
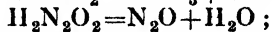
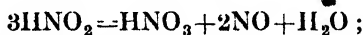


Hydroxyl-  
amine.

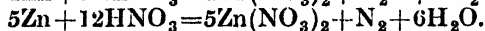
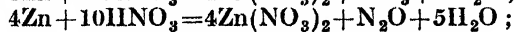
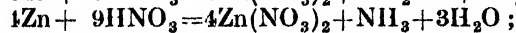


Ammonia.

The production of hydroxylamine and ammonia occurs chiefly with tin and zinc, although under suitable conditions other metals may give traces. The nature and quantity of both primary and secondary products depend upon the concentration of the acid. Secondary products result from the following reactions :—



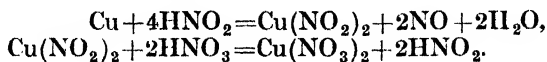
Thus the reduction products of nitric acid produced by zinc under various conditions may be shown in the following reactions :—



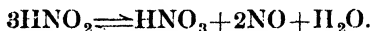
Veley<sup>1</sup> suggests that nitrous acid is necessary to initiate the reaction between all metals and nitric acid, and his experiments go to prove that really pure nitric acid has no action on pure metals. There is considerable difficulty in obtaining complete purity of the reacting substances, and traces of nitrous acid are produced probably by electrolytic action set up by the most minute quantities of impurities in the metals. The very slight action of pure nitric acid of 30 per cent. concentration on pure metals was almost entirely prevented if the metals were agitated in the solution, because it was not possible for nitrous acid to concentrate round the metal. No action occurred at all if the formation of nitrous acid was inhibited by adding such substances as urea, hydrogen

<sup>1</sup> Veley, *Proc. Roy. Soc.*, 1890, 46, 216; 1893, 52, 27; *Phil. Trans.*, 1891, 182A, 279; *J. Soc. Chem. Ind.*, 1891, 10, 204.

peroxide, potassium chlorate, etc. While Veley agrees that the metals copper, silver, mercury, and bismuth differ in their action from the rest of the metals, yet he maintains that in all cases nitrous acid is necessary to start the reaction, and that nitrous acid is the primary product in all cases. Thus, in the case of copper the reaction can be represented by the equations



The decomposition or formation of nitrous acid is shown by the reversible reaction



In the case of both classes of metals Veley found that rapid solution occurred in nitrous acid, less rapid in a mixture of nitrous and nitric acids, and much slower action still in the case of pure nitric acid solution.

Higley<sup>1</sup> has investigated the action of nitric acid on iron, and also the electrolytic reduction of nitric acid. The products of the reaction in each case are closely comparable. Thus, in the electrolytic reduction of nitric acid, ammonia and nitric oxide are the chief products of dilute acids, while hydrogen is also produced. Increasing concentration of the acid yields correspondingly larger amounts of nitrogen peroxide.

In the case of the reduction by iron, the products are ammonia, nitric oxide, and nitrogen peroxide, and while there is no free hydrogen, yet there are considerable amounts of nitrogen and nitrous oxide. Very weak acid yields large quantities of ammonia, but nitrogen peroxide is practically the only product with concentrated acid.

The only metal which produces free hydrogen is magnesium, and the nitric acid must be very dilute. As magnesium is next to the alkali metals with regard to its high solution tension, Webb<sup>2</sup> suggests that hydrogen is liberated first by all metals with a higher solution tension than hydrogen, while those with a lower solution tension (copper, mercury, silver) are polarised in a solution of nitric acid. The function of nitrous acid in starting the reaction between these metals and nitric acid is that of a depolariser.

Very few metals can be used as containers, etc., for nitric acid, but aluminium seems to have possibilities in this respect, and the action of nitric acid on this metal has received much attention.<sup>3</sup> Temperature and concentration are the chief factors, and it would seem that aluminium can be used at low temperatures for either very weak or very concentrated acids. Extensive use is made of aluminium air-elevator pipes at Notodden in Norway in connection with the absorption system for nitric acid produced by the arc process.

Generally speaking, the action of nitric acid upon alloys is of a very varied and complex nature.<sup>4</sup> One of the commonest substances used for handling and storing nitric acid is iron containing varying amounts of silicon (12 to 20 per cent.). Narki, ironac, and tantiron are examples of

<sup>1</sup> Higley, *Amer. Chem. J.*, 1893, 15, 71; 1895, 17, 18; 1896, 18, 587; 1899, 21, 377.

<sup>2</sup> Webb, *Absorption of Nitrous Gases* (Arnold, 1923), p. 68.

<sup>3</sup> Trillat, *J. Soc. Chem. Ind.*, 1915, 34, 874; Seligman and Williams, *ibid.*, 1916, 35, 665.

<sup>4</sup> Montemartini, *Gazzetta*, 1892, 22, 250, 277, 397, 426; *Atti R. Accad. Lincei*, 1892, [5], 1, 1, 63; 1908, 27, 366; 1909, 28, 272; 1913, 32, 311, 1135; Stansbie, *J. Soc. Chem. Ind.*, 1906, 25, 45, 1071.

silicon-iron alloys which are used alternatively to stoneware for towers, pumps, fans, etc., in various absorption systems.

**Detection and Estimation.**—Free nitric acid is detected by the ready production of brown fumes when warmed with metallic copper. Nitrates behave similarly when treated with concentrated sulphuric acid and copper.

The brown-ring test consists in adding a solution of ferrous sulphate to the solution of nitric acid or nitrate, and carefully pouring concentrated sulphuric acid down the side of the test-tube. The strong acid collects at the bottom of the tube, and at the junction of the two liquids a brown ring is formed containing the compound  $\text{FeSO}_4 \cdot \text{NO}$ .

Brucine, in the presence of concentrated sulphuric acid, develops a red colour.

"Nitron" gives a white precipitate with nitric acid or nitrates; the test is sensitive to 1 part per 60,000.

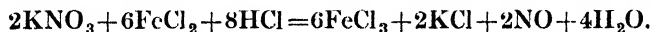
**Estimation.**—There are a large number of methods in use for estimating nitric acid and nitrates. The more important of these methods may be classified as follows:—

1. *Titration Methods.*
2. *Gasometric Methods.*
3. *Gravimetric Method.*

1. *Titration Methods.*—(a) The simplest method of estimation of free nitric acid is by titrating with standard alkali. Any indicator may be used in the absence of nitrous acid, but if this is present, then methyl red is preferable, as it is only slowly acted upon.<sup>1</sup>

(b) The Bowman and Scott<sup>2</sup> method consists in reducing the nitric acid (or nitrate) to  $\text{N}_2\text{O}_3$  by means of a solution of ferrous sulphate in strong sulphuric acid, the end point being indicated by the appearance of a pinkish-brown coloration. Nitrous acid and nitrites do not interfere, but chlorates, bromates, iodates, chlorides, bromides, and iodides must be absent.

(c) The Pelouze-Fresenius method is based upon the reduction of nitrate by means of ferrous chloride, and the estimation of the excess of ferrous salt by titration with standard potassium permanganate:



This method appears to be accurate with dilute solutions of nitrates.<sup>3</sup>

(d) Many modifications of the reduction of nitrates to ammonia have been proposed. The original method was by heating the nitrate with Devarda's alloy in alkaline solution, and subsequently distilling the ammonia into standard acid solution.

Other reducing agents are, reduced iron and sulphuric acid,<sup>4</sup> aluminium amalgam in alkaline solution,<sup>5</sup> and titanous sulphate.<sup>6</sup> The last-named method has the advantage of quickness with accuracy. Nitrates can also be estimated by the electrolytic reduction in a solution of copper sulphate containing a known quantity of standard acid.<sup>7</sup>

<sup>1</sup> Koehler, Marquayrol, and Jovinet, *Ann. Chim. anal.*, 1913, 18, 45.

<sup>2</sup> Bowman and Scott, *J. Ind. Eng. Chem.*, 1915, 7, 766.

<sup>3</sup> Letts and Rea, *Proc. Roy. Soc. Edin.*, 1915, 35, 168.

<sup>4</sup> Lunge and Keane, *Technical Methods of Chemical Analysis*.

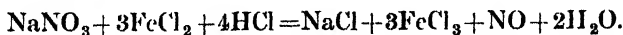
<sup>5</sup> Pozzi Escott, *Zeitsch. angew. Chem.*, 1911, 43, 2046.

<sup>6</sup> Knecht, *J. Soc. Chem. Ind.*, 1915, 34, 126.

<sup>7</sup> Vortmann, *Ber.*, 1890, 23, 2790; Easton, *J. Amer. Chem. Soc.*, 1903, 25, 1042; Ingham, *ibid.*, 1904, 26, 1251.

2. *Gasometric Methods.*—(a) The Lunge nitrometer is very largely used for the estimation of nitric acid and nitrates, but is liable to a number of errors due to the solubility of nitric oxide in sulphuric acid, temperature fluctuations, period of shaking, etc.<sup>1</sup>

(b) The Schloesing-Grandcau method depends upon the reduction of nitrates to nitric oxide (which is measured) by boiling with ferrous chloride and hydrochloric acid :



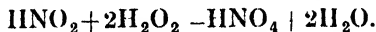
3. *Gravimetric Method.*—Nitron has already been mentioned as affording a delicate means of detecting nitrates. This substance is 1 : 4 diphenyl, 3 : 5 endoanilido, 4 : 5 dihydro, 1 : 2 : 4 triazole, and gives a crystalline insoluble nitrate even with minute quantities of nitric acid.<sup>2</sup> The precipitate obtained by using an acetic acid solution of nitron is filtered and weighed in a Gooch crucible.

Nitrous and nitric acids in a mixture may be estimated by first estimating the nitrous acid by means of potassium permanganate, and then oxidation of the nitrous acid in another portion with hydrogen peroxide and estimating the total nitric acid with nitron.<sup>2</sup>

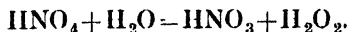
The nitron method for nitrates is inapplicable in the presence of hydrobromic, hydriodic, chloric, perchloric, thiocyanic, ferrocyanic, ferrieyanic, and picric acids.

#### PERNITRIC ACID, $\text{HNO}_4$ .

The supposed nitrogen hexoxide was considered to give a pernitric acid with water. Oxidation of nitrous acid in solution by 3 per cent. hydrogen peroxide solution is stated by Raschig<sup>3</sup> to produce pernitric acid :



The decomposition of pernitric acid by water occurs slowly, according to the reaction



Pure hydrogen peroxide and nitrogen pentoxide at low temperatures yield a substance exhibiting typical properties of a per-acid :<sup>4</sup>



Bromine is liberated from potassium bromide, and aniline is oxidised to nitroso-benzene by the acid.

Electrolysis of a solution of silver nitrate yields a black crystalline precipitate, assumed to be the silver salt of pernitric acid.<sup>5</sup>

<sup>1</sup> Tower, *Zeitsch. anorg. Chem.*, 1906, 50, 382; Marquoyrol and Florentin, *Bull. Soc. chim.*, 1911, 9, 231; Taylor and Webb, *J. Soc. Chem. Ind.*, 1922, 41, 362T; Newfield and Marsh, *J. Amer. Chem. Soc.*, 1906, 28, 877; Leo, *Chem. Zeit.*, 1909, 33, 1218.

<sup>2</sup> Busch, *Ber.*, 1905, 38, 861; 1906, 39, 1401.

<sup>3</sup> Raschig, *Zeitsch. angew. Chem.*, 1904, 17, 1419.

<sup>4</sup> d'Ans and Friederich, *Zeitsch. anorg. Chem.*, 1911, 73, 344.

<sup>5</sup> Mulder and Herringe, *Rec. Trav. chim.*, 1898, 17, 129.

## CHAPTER XIII.

### NITROGEN AND SULPHUR.

NITROGEN combines with sulphur indirectly, usually by coupled reactions, giving a solid compound,  $S_4N_4$ , a liquid,  $S_5N_3$ , and possibly other compounds. These are probably nitrides of sulphur; the nitrogen is the electro-negative part, as is shown by the manner of formation and the reactions. They can be regarded as derivatives of ammonia, from which they are formed by some remarkable reactions.

**Solid Sulphur Nitride.**—The solid nitride was discovered by Gregory<sup>1</sup> in 1835, and then completely investigated by a number of scientists.<sup>2, 3</sup>

The preparations follow three main lines:

1. *From Chlorides of Sulphur, or Thionyl Chloride, and Ammonia in an Organic Solvent.*—The liquid medium in which the reaction takes place may be carbon disulphide,<sup>4</sup> benzene,<sup>5, 6</sup> or chloroform.<sup>7</sup> A solution containing 25 grams of  $SCl_2$  in 200 c.c. of benzene is saturated with ammonia.<sup>5</sup> The orange-coloured precipitate is washed with water to free it from ammonium chloride and recrystallised from carbon disulphide, or carbon tetrachloride, to free it from sulphur. It crystallises on cooling in golden crystals. A further quantity is obtained by evaporation of the benzene mother-liquor, and may be recrystallised from benzaldehyde.

It is probably formed by the reaction



The yield actually obtained exceeds that calculated from this equation by about 10 per cent. This is attributed to the reaction between  $S_2Cl_2$  and  $NH_3$ , as stated below.

When sulphur monochloride, ( $S_2Cl_2$ ), is used, there is an abundant separation of sulphur. By mixing ice-cold solutions of ammonia and of sulphur monochloride, both in chloroform, there is obtained a mixed precipitate, probably formed by the equation



Other sulphides are found in the mother-liquor.<sup>9</sup>

<sup>1</sup> Gregory, *J. Pharm.*, 1835, 21, 315; 22, 301.

<sup>2</sup> Soubciran, *Ann. Chim. Phys.*, 1838, [2], 67, 71, 96.

<sup>3</sup> Fordos and Gelis, *Compt. rend.*, 1850, 31, 702.

<sup>4</sup> Muthmann and Clever, *Ber.*, 1896, 29, (i), 341; (Clever and Muthmann, *Zeitsch. anorg. Chem.*, 1896, 13, 200.

<sup>5</sup> Divers and Haga, *Chem. News*, 1896, 74, 277.

<sup>6</sup> Schenk, *Annalen*, 1896, 290, 171.

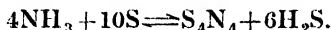
<sup>7</sup> Macbeth and Graham, *Proc. Roy. Irish Acad.*, 1923, 36, 31.

<sup>8</sup> Ruff, *Ber.*, 1904, 37, 1573.

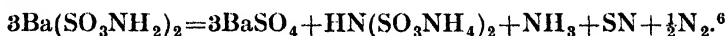
<sup>9</sup> Macbeth and Graham, *loc. cit.*; Valkenburgh and Bailar, *J. Amer. Chem. Soc.*, 1925, 47, 2134.

Thionyl chloride gives a mixture of  $S_4N_4$ , ammonium chloride, and ammonium salts of thionic acids.<sup>1</sup>

2. *From Liquid Ammonia and Sulphur*.—Sulphur dissolves freely in liquid ammonia, giving a red-brown solution,<sup>1, 2, 3</sup> and the probability that a chemical reaction takes place was pointed out.<sup>4</sup> It was likewise shown<sup>5</sup> that, after the addition of AgI to remove the  $H_2S$ , and removal of the  $Ag_2S$  by filtration, the subsequent evaporation of the ammonia from the filtrate yields  $S_4N_4$ . The evaporation of a solution containing both  $H_2S$  and  $S_4N_4$  in  $NH_3$  leaves pure sulphur. These facts, taken together, point to the establishment of an equilibrium. Thus :



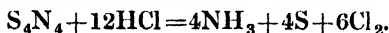
3. *From Barium Amido-sulphonate*.—This salt decomposes on heating, giving various products, among which an orange sublimate was found of empirical composition  $NS$ , formed probably according to the equation



*Properties*.—The compound forms reddish crystals which belong to the rhombic,<sup>7</sup> or monoclinic<sup>8</sup> systems. The density is 2.2. Under atmospheric pressure it sublimes at  $135^\circ C.$ , while under increased pressure it melts at  $178^\circ C.$ <sup>9</sup> When sublimed in a vacuum over silver gauze it condenses as a blue substance, which may be a polymer.<sup>10</sup> It decomposes slowly when heated to  $185^\circ C.$ , and over  $200^\circ C.$  explodes, giving nitrogen, sulphur, and possibly another sulphide. It is an endothermic compound,<sup>11</sup> the heat of formation being  $-0.7007$  Cals. per gram, or  $-129$  Cals. per mol.,  $S_4N_4$ . It is insoluble in water, but soluble in the solvents mentioned above, in alcohol, ether, and many other solvents. The molar weight in these corresponds to the formula given,<sup>9, 12, 13</sup> e.g. by the ebullioscopic method in  $CS_2$ .

*Reactions*.—The compound is slowly hydrolysed by hot water, more quickly by alkalis and acids, giving ammonia or its salts, and salts of sulphur oxy-acids or free sulphur. These reactions prove that it is a *nitride of sulphur*, not a *nitrogen sulphide*.

It is decomposed by dry hydrogen chloride, according to the equation



With liquid hydrogen chloride it gives ammonium chloride and chlorides of sulphur.<sup>5</sup> It forms many addition compounds: thus  $S_4N_4.2NH_3$  can be obtained from the solution in liquid ammonia,

<sup>1</sup> Gore, *Proc. Roy. Soc.*, 1873, 21, 140.

<sup>2</sup> Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 821.

<sup>3</sup> Hugot, *Ann. Chim. Phys.*, 1900, [7], 21, 5.

<sup>4</sup> Moissan, *Compt. rend.*, 1901, 132, 510.

<sup>5</sup> Ruff and Geisel, *Ber.*, 1905, 38, 2659.

<sup>6</sup> Divers and Haga, *Chem. News*, 1896, 74, 277; *Trans. Chem. Soc.*, 1896, 69, 1652.

<sup>7</sup> Nicklès, *Ann. Chim. Phys.*, 1851, [3], 32, 420.

<sup>8</sup> Artini, *Zeitsch. Kryst.*, 1906, 42, 68.

<sup>9</sup> Schenck, *Annalen*, 1896, 290, 171; Andreocci, *Zeitsch. anorg. Chem.*, 1897, 14, 246.

<sup>10</sup> Burt, *Trans. Chem. Soc.*, 1910, 97, 1171.

<sup>11</sup> Berthelot and Vieille, *Ann. Chim. Phys.*, 1882, [5], 27, 202; *Compt. rend.*, 1881, 92, 130.

<sup>12</sup> Muthmann and Clever, *Ber.*, 1896, 29, (i), 340; 1897, 30, (i), 627.

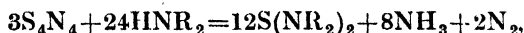
<sup>13</sup> Andreocci, *loc. cit.*

$S_4N_4Cl_4$  and  $S_4N_4Br_4$  are yellow and red substances respectively, and  $S_4N_4SCl_2$  is a yellow substance. These compounds are prepared by the addition of the respective elements and  $SCl_2$  to  $S_4N_4$  in solution.

Many compounds with acid radicals, such as  $NSO$  and  $S_4N_3Cl$ , have been prepared;<sup>1,2</sup> the latter substance by the reaction between  $S_4N_4$  and sulphur chloride or acetyl chloride. It behaves like a base, giving salts, *e.g.* a nitrate with nitric acid.<sup>3</sup>

*Constitution.*—The preparation from  $SCl_2$  and  $NH_3$ , and the decomposition with  $HCl$  into ammonia and sulphur, show that the sulphur takes the place of the hydrogen of  $NH_3$ , and that the nitrogen atoms are not linked together but are united to sulphur by 12 valencies. The valency of the sulphur is probably greater than 3—that is, it may be 4.

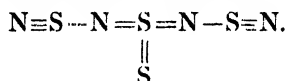
Further, in the formation of thiodiamines from secondary amines by the equation



the average valency of each sulphur atom exerted towards  $-NR_2$  has fallen to 2, so that the hydrogen of the amine is insufficient to give ammonia, and nitrogen is set free. A solution in liquid ammonia reacts with lead iodide to give  $PbN_2S_2$ , with mercuric iodide to give  $HgN_2S$ ; in which, as shown by their decomposition when acted on by  $HCl$ , the metal is united to nitrogen but not to sulphur. They are therefore considered to be the dithiodi-imide and the thiodi-imide res-

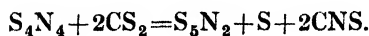
spectively, and to contain the radicals  $S=S \begin{matrix} \diagup N- \\ \diagdown N- \end{matrix}$  and  $-N=S=N-$ .

The structure assigned to the compound  $S_4N_4$  is :



On sublimation of nitrogen sulphide with sulphur, small quantities of a dark red liquid are obtained which solidifies at  $-80^\circ C.$ , and on analysis gives data corresponding to the empirical formula  $NS_2$ .<sup>4</sup>

**Liquid Pentasulphur Dinitride.**—This compound is prepared by the reaction between the solid sulphide and carbon disulphide under pressure at  $100^\circ C.$ :<sup>5</sup>



It is also found in the mother-liquors, resulting from the preparation of  $S_4N_4$ , and in the products of its decomposition by heat. It is a red mobile liquid of density 1.9, which is easily frozen; the solid melts at about  $10^\circ C.$  It can be vaporised with partial decomposition. Like the solid nitride, it is soluble in organic solvents and insoluble in water, aqueous acids, and alkalis, by which, however, it is hydrolysed, giving ammonia and sulphur. It can be kept in solution. The liquid itself decomposes slowly and explodes on heating.

<sup>1</sup> Demarcay, *Compt. rend.*, 1880, **91**, 854, 1066.

<sup>2</sup> Muthmann and Clever, *loc. cit.*

<sup>3</sup> Muthmann and Seitter, *Ber.*, 1897, **30**, 627.

<sup>4</sup> Usher, *Trans. Chem. Soc.*, 1925, **127**, 730.

<sup>5</sup> Muthmann and Clever, *Zeitsch. anorg. Chem.*, 1897, **13**, 200.



## CHAPTER XIV.

### FIXATION OF NITROGEN

**Arc Processes.**—The combination of nitrogen and oxygen by electric sparks was first shown by Cavendish in 1784. Rayleigh<sup>1</sup> in 1897, describing his experiments which isolated argon from the atmosphere, pointed out the possibilities of utilising the electric arc for the industrial fixation of nitrogen.

The conditions for production of a good yield of nitric oxide are :

1. The maintenance of a high-tension arc.
2. The exposure of a large quantity of air to electrical action.
3. The rapid chilling of the products.<sup>2</sup>

The first technical attempt to utilise this reaction was that of Bradley and Lovejoy<sup>3</sup> in 1902 at Niagara. The arcs were struck between platinum points fixed in an outer casing and similar points which were rapidly rotated on a concentric axle, resulting in the making and breaking of over 400,000 arcs per minute. Although the efficiency was good, the yield being 86 grams of nitric acid per K.W.H., it was found that the mechanism was too complicated for technical use.

*The Birkeland-Eyde Arc.*—The first commercially successful process was that of Birkeland and Eyde,<sup>4</sup> which was started in 1903 at Notodden in Norway. An alternating current arc struck between water-cooled copper electrodes is deflected by a powerful magnetic field applied in a direction at right angles to that containing the electrodes. The arcs formed across the shortest air space are driven outwards in the form of a semicircle until their resistance becomes so great that they are extinguished, or until the direction of the current changes so that the arcs are directed to the other side. The result is a disc of electric flame or an electric "sun," two yards in diameter, formed in a firebrick chamber through which the air, preheated in the outer part of the furnace, is blown. The percentage of nitric oxide in the issuing gases is about 1.25, and the yield of nitric acid 67 grams per K.W.H., or 580 to 590 kilograms per K.W.Y. (reckoned as acid and nitrate). Originally about 700 K.W. were employed in the furnaces, but 4000 K.W. are now used. The voltage employed is about 5000, of which up to 4000 are across the arc, the remainder being used in the inductances, which are necessary to steady the arc. The power consumed is great, so that the process is only applicable where power is cheap, e.g. derived from water, as at Notodden. In these localities, the simple nature of the process and the robustness of the plant, combined with the fact that the raw

<sup>1</sup> Rayleigh, *Trans. Chem. Soc.*, 1897, 71, 181.

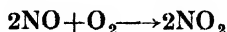
<sup>2</sup> See also section on Synthesis, under Nitric Oxide, p. 159.

<sup>3</sup> Bradley and Lovejoy, *English Patent*, 8230 (1901); Haber, *Zeitsch. Elektrochem.*, 1903, 9, 381.

<sup>4</sup> *Zeitsch. Elektrochem.*, 1905, 11, 252; Birkeland, *Trans. Faraday Soc.*, 1906, 2, 98; Eyde, *J. Roy. Soc. Arts*, 1909, 57, 568; 1912, 60, 645; Scott, *ibid.*, 1912, 60, 645.

material—air—costs nothing, have allowed it to retain its position in the manufacturing world.

The gases escaping from the furnace, which have rapidly cooled to a temperature of about  $800^{\circ}$  to  $1000^{\circ}$  C., are used for steam-raising. At  $600^{\circ}$  C. the reaction



begins, and is complete at  $140^{\circ}$  C. The process of cooling from  $800^{\circ}$  to  $175^{\circ}$  C. is used to preheat the entering air. The oxides of nitrogen, after cooling to  $50^{\circ}$  C. by passing through water-cooled aluminium pipes, pass into a cylinder lined with acid-proof stone in order to carry further the (slow) conversion into  $\text{NO}_2$ . These oxides are then absorbed by water trickling over broken quartz in granite towers 70 feet high and 20 feet in diameter. The acid produced in the first tower reaches a

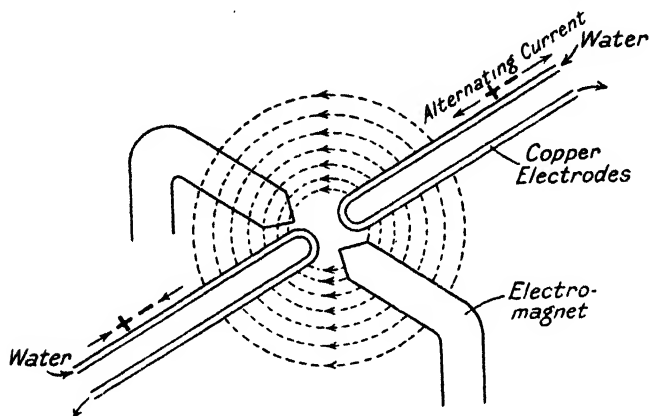


FIG. 22.—Birkeland-Eyde furnace.

concentration of 30 to 40 per cent. of nitric acid, while the strengths in the succeeding towers are 20, 10, and 5 per cent. respectively. The maximum production of nitric acid corresponds to the reaction



which only takes place in cold dilute solution. In the case of hot solutions containing more than 46 per cent.  $\text{HNO}_3$ , and gases containing about 1 per cent.  $\text{NO}$ , the nitrous acid is decomposed :



Hence in practice some  $\text{NO}$  will escape, and this after further oxidation is absorbed by solutions of sodium hydroxide or sodium carbonate, or a mixture of both, when about 95 per cent. of the  $\text{NO}$  appears as sodium nitrite and 5 per cent. as the nitrate. Evaporation of the solution produces the crystalline mixture, which is used in the chamber process for sulphuric-acid manufacture, or else the nitrite is recovered for the manufacture of dyes.

The nitric acid may be concentrated according to the methods detailed on p. 190, or used (as in Norway) to dissolve limestone. The normal calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , is converted into a basic salt, containing 13 per cent. of nitrogen, which is not deliquescent and is used

as a fertiliser. Calcium nitrite,  $\text{Ca}(\text{NO}_2)_2$ , containing 21.2 per cent. of nitrogen, may easily be made from the gases containing excess of nitric oxide.

*The Pauling Furnace.*—The first technical installation of the Pauling process was erected at Innsbruck in 1909, following experiments which began in 1906.<sup>1</sup> Steel water-cooled electrodes, bent away from each other in the shape of a V, are employed, and the arc is kept at high tension by a blast of air. The alternating arcs, struck between ignition knives of iron which pass through the electrodes, are carried upwards by the blast of air, giving a fan-shaped electric flame of a high temperature. The gases leaving at about  $1000^\circ \text{C.}$  contain about 0.8 per cent. of nitric oxide, which corresponds to 60 grams of  $\text{HNO}_3$  per K.W.H. or 525 kilograms K.W.Y.

The modification of Rossi,<sup>2</sup> who substituted electrodes of aluminium

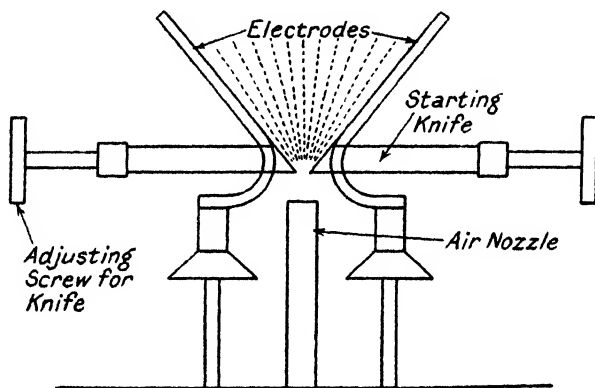


FIG. 23.—Pauling furnace.

alloyed with barium and lead, greatly improved the yield, as particles of iron are found to decompose the nitric oxide catalytically.

*The Schönherr Furnace.*—The arc process devised by Schönherr and Hessberger in 1905<sup>3</sup> also depends upon the fact that an arc may be carried by a current of heated air. This is supplied not across the discharge, giving a series of rapidly extinguished arcs, but along it, giving a single high-tension arc which is in contact with the air for over a long distance. The furnace is in the form of a cylinder, 20 to 25 feet long, made of iron lined with firebrick, in the centre of which is one electrode consisting of an iron tube, a few inches in diameter, water-cooled at its top end. At the lower end another insulated electrode is enclosed in a water-cooled copper block. The arc, first struck at the bottom, is carried up spirally by the air, which is supplied through holes bored tangentially to the furnace walls. The air is regulated so that the upper end of the arc is made on the water-cooled end of the tube electrode.

The furnace, supplied by a 3-phase alternating current, may take from 700 to 1000 K.W. and about 3500 volts and 290 ampères. The air is

<sup>1</sup> Russ, *Zeitsch. Elektrochem.*, 1909, 15, 544; Pauling, *ibid.*, 1911, 17, 431.

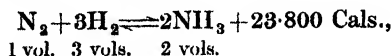
<sup>2</sup> Rossi, *English Patent*, 23959 (1913); also *U.S. Patent*, 1115627 (1914).

<sup>3</sup> Schönherr, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 131.

preheated to about  $500^{\circ}\text{C}$ . by the issuing gases, and leaves the furnace at about  $850^{\circ}\text{C}$ . with a content of about 1.8 per cent. of nitric oxide. The yield is 68 grams of  $\text{HNO}_3$  per K.W.H., or 500 to 600 kilograms per K.W.Y.

*Absolute and Comparative Efficiency of Electrical Processes for the Combustion of Nitric Oxide.*—The proportions of the total electrical energy supplied which are used in the actual production of nitric oxide are small. If all the electrical energy were so used in the form of heat to combine nitrogen and oxygen, which have a heat of combination equal to 21,600 Cals., it can easily be shown<sup>1</sup> that 1 K.W.H. should give as a maximum 2500 grams  $\text{HNO}_3$ . The amounts given above are about 3 per cent. of this. But the electrical energy is also required to heat up a large excess of air (with 1.25 per cent. of  $\text{NO}$ ) to, say,  $900^{\circ}\text{C}$ ., and if this heat is included, the theoretical yield is only 102 grams  $\text{HNO}_3$  per K.W.H., or the efficiency is over 60.

*Synthetic Ammonia.*—The fixation of atmospheric nitrogen in the form of ammonia by direct combination with hydrogen is one of the most successful and economical of processes, as the amount of energy required is small. The fact that about 65 per cent. of the world's supply of fixed nitrogen is produced by this method (1925) is an indication of the importance of this process. The direct combination of nitrogen and hydrogen in the presence of a catalyst is shown by the equation



and the equilibrium of this reversible reaction is given by the expression

$$K = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^1 P_{\text{H}_2}^3}.$$

[For further details on equilibria, velocities, and yields, see section on  $\text{N}_2$ ,  $\text{H}_2$  Equilibria, pp. 95 *et seq.*]

It is obvious from the above equation that, as a contraction in volume from 4 vols. to 2 vols. occurs, increase of pressure will favour the

<sup>1</sup> Allmand and Ellingham, *Applied Electrochemistry* (Arnold, 1924).

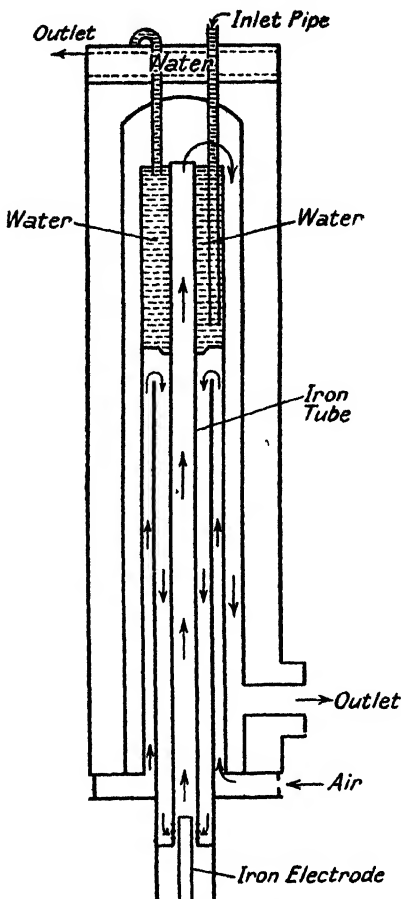
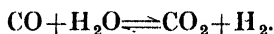


FIG. 24.—Schönherr-Hessberger furnace.

formation of ammonia; also as the reaction is exothermic, as low a temperature consistent with other factors will give the best yield (p. 97).

*Haber Process.*—In the “Haber” process, the first to achieve technical success, the nitrogen and hydrogen are brought into contact with the catalyst at a pressure of 200 atmospheres and a temperature of 600° C. The catalyst most generally used is iron in some form or other, although this is not necessarily the best catalyst apart from the question of cost. The various catalysts have already been discussed under Ammonia (p. 103). In any case, whatever the catalytic material used, it is imperative in the Haber process that the reacting gases shall be as pure as possible. It is estimated that from 70 to 75 per cent. of the working cost of the plant is in the production of pure nitrogen and hydrogen.

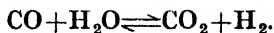
In Germany there are two methods of obtaining the nitrogen-hydrogen mixture, and both processes involve the so-called “Bosch” purification methods. At Oppau, water-gas (hydrogen 50 per cent., carbon monoxide 40 per cent., carbon dioxide and nitrogen) is mixed with steam and air, and the mixture passed over a heated catalytic material of ferric oxide and nickel or chromium oxide. The chief reaction is that between the steam and carbon monoxide, resulting in the production of hydrogen and carbon dioxide:



At comparatively low temperatures, namely, 400° to 600° C., the reaction proceeds to a considerable extent from left to right, and the resulting gas now contains nitrogen, hydrogen, carbon dioxide, and small amounts of carbon monoxide, hydrogen sulphide, argon, and hydrocarbons. Carbon dioxide is removed by washing with water at high pressure; carbon monoxide is absorbed by scrubbing with ammoniacal cuprous formate, followed by hot caustic soda solution, which also removes the hydrogen sulphide.

The nitrogen-hydrogen mixture is now brought up to the required ratio 1 : 3 by the addition of nitrogen from a Linde plant.

At Merseberg, the “Haber-Bosch”<sup>1</sup> process differs from that in use at Oppau, in that the addition of pure nitrogen is dispensed with. Water-gas is mixed with producer gas<sup>2</sup> (chiefly nitrogen and carbon monoxide) and steam, and the mixture passed through similar contact furnaces as at Oppau to oxidise the carbon monoxide to the dioxide:



The carbon dioxide, carbon monoxide, and sulphuretted hydrogen are removed as before, and a final removal of impurities is effected by passing through a series of small contact furnaces. It is thus possible to obtain finally the right nitrogen and hydrogen mixture by suitable adjustment of the original amounts of water-gas, producer gas, and steam. Or nitrogen and steam may be passed over iron.<sup>3</sup> The theoretical considerations underlying the combination of nitrogen and

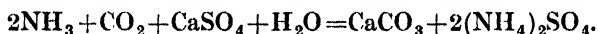
<sup>1</sup> *English Patent*, 16209 (1920).

<sup>2</sup> Coke-oven gas may be used (Dodge, *Chem. Met. Eng.*, 1926, 33, 416).

<sup>3</sup> Blackburn and Thomas, *English Patent*, 257689 (1926).

hydrogen have been dealt with in the section on the ammonia-nitrogen-hydrogen reaction and equilibrium, and it is only necessary here to indicate the technical working of the Haber process.

The purified mixture of nitrogen and hydrogen in the proportion of one to three is passed into the circulatory system through a soda-lime drier. The gases under a pressure of 200 atmospheres are pre-heated by electrical coils, and come into contact with the catalyst which is contained in steel bombs, 6 metres by 80 cm. internal dimensions.<sup>1</sup> The catalyst material is maintained at 600° C. by means of a system of heat regenerators, and the ammonia is absorbed by water under pressure flowing down steel spirals. A solution containing about 25 per cent. of ammonia is obtained, and the uncombined nitrogen and hydrogen are passed back into the circulatory system after drying. This ammonia liquor is either used for oxidation direct to nitric acid (p. 214), or else converted into ammonium sulphate by neutralisation with sulphuric acid. This latter substance became very scarce in Germany during the War owing to the blockade of the Allies, which cut off the supply of pyrites. This shortage of sulphuric acid was overcome to a large extent by the successful technical process of the Badische Company.<sup>2</sup> Ammonia gas and carbon dioxide are passed simultaneously into water which contains freshly calcined gypsum in suspension. Calcium carbonate is precipitated and ammonium sulphate remains in solution :



A highly purified ammonium sulphate is obtained by concentrating the filtrate in vacuum pans.

An interesting modification of the Haber process was tried at Sheffield, Alabama, by the United States Government Nitrate Factory No. 1, under various patents of the General Chemical Company.<sup>3</sup> The catalyst used was an activated sodamide made by heating to 550° C. pumice impregnated with nickel or ferric nitrate, and treating at 450° C. with sodium and ammonia, when sodamide was formed in the spongy metal. The nitrogen-hydrogen mixture, at the relatively low pressure of 70 to 100 atmospheres, was passed over the catalytic material maintained at a temperature of 500° C. This process was not a technical success owing to the faulty construction of the plant and the poisoning of the catalyst with water. Later the process was taken over by the Atmospheric Nitrogen Company in conjunction with the Solvay Company of New York, and a successful production of 10 tons of liquid ammonia per day for refrigerator purposes was attained.

*The Claude Process.*—M. Georges Claude<sup>4</sup> carefully investigated the equilibrium percentages of ammonia produced at very much higher pressures than those used by the Badische Company in the Haber process, and in 1918 announced his invention by which the use of pressures of 1000 atmospheres very materially increased the yield of ammonia. Under a pressure of 1000 atmospheres and temperature of 600° C. the

<sup>1</sup> For diagrams of catalyst bombs, see p. 105.

<sup>2</sup> Wolf, *German Patent*, 299752 (1919); Badische Company, *German Patent*, 300724 (1920).

<sup>3</sup> General Chemical Company, *United States Patents*, 1141947 and 1141948 (1915); *English Patents*, 120546, 124760, 124761, 124762 (1918).

<sup>4</sup> Claude, *Compt. rend.*, 1919, 169, 649, 1039; 1920, 170, 174; *English Patents*, 130086 (1918), 142150 (1918).

percentage of ammonia reaches the high figure of 25, whereas from the table on p. 99 it will be seen that only 8.25 per cent. of ammonia is given at the same temperature under 200 atmospheres. In addition to the enhanced yield there are important economies effected in the working of the plant, as in the Haber process the maintaining and restoring of pressure by stages is troublesome and expensive compared with the actual yield of 6 per cent. of ammonia. In the Claude process the work of compression is greater, but since it is proportional to the logarithm of the pressure ratio  $\left(A = RT \log \frac{p_2}{p_1}\right)$ , it is only greater in the proportion 2.3 to 3.

The pressure is obtained in stages of 100—300 1000 atmospheres, and the advantages of the process are :

(1) A sufficient percentage conversion can be obtained in one operation, instead of a lengthy series of circulations as at 200 atmospheres.

(2) Liquid ammonia is produced in bulk merely by releasing the pressure to that of the atmosphere and cooling with water.

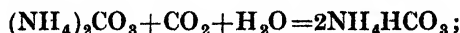
(3) The spontaneous evaporation of ammonia from the liquid state at ordinary temperatures obviates the expense of evaporation as required by the Haber process.

(4) A useful source of refrigeration is provided in converting the liquefied ammonia into gas, which can be utilised for subsequent fixation of nitrogen as a fertiliser.

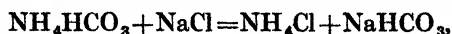
The second important feature of this process, due to Schreib,<sup>1</sup> is the fixing of the ammonia in the form of ammonium chloride. It would appear that this salt is just as efficient a fertiliser as the sulphate, and could be obtained in larger bulk more cheaply. The ammonium chloride is obtained by a modification of the Solvay (ammonia-soda) process. Saturated sodium chloride solution is further saturated with ammonia gas under pressure and carbon dioxide is passed into the solution, with the formation of ammonium chloride and sodium bicarbonate,



The sodium bicarbonate, being practically insoluble in sodium chloride solution, is precipitated, and the filtrate is again saturated by the addition of solid sodium chloride. Further treatment with ammonia and carbon dioxide produces normal ammonium carbonate in solution and precipitates ammonium chloride. The ammonium carbonate in solution is converted by a further quantity of carbon dioxide into the bicarbonate,



and this ammonium bicarbonate precipitates sodium bicarbonate,



giving a solution of ammonium chloride as in the first reaction.

Hence a cycle of operations occurs with alternate precipitation of sodium bicarbonate and ammonium chloride. This latter salt is obtained 97 per cent. pure in two cycles, and as the impurity is chiefly sodium chloride, the ammonium chloride can be directly used as a fertiliser without injurious effects.

<sup>1</sup> Schreib, *German Patent*, 36093 (1885).

The chief source of hydrogen for the Claude process, as worked in France, is coke-oven gas, and one of the most promising methods for purification is by fractionation between  $-160^{\circ}\text{C}$ . and  $-210^{\circ}\text{C}$ ., whereby hydrogen is obtained suitable for the ammonia synthesis.<sup>1</sup> According to Cederberg,<sup>2</sup> efficient purification of hydrogen from oxygen, water-vapour, carbon monoxide, and dioxide can be obtained by passing the gases through a solution of sodium in liquid ammonia. Of the various catalysts used, a material which will last for some hundreds of hours has been obtained by directing a jet of oxygen into a molten mass of ferrous oxide, iron, calcium oxide, and a small amount of alkaline oxide contained in a magnesia crucible.<sup>3</sup>

*Casale Process.*—The outstanding feature of the Casale<sup>4</sup> process for synthetic ammonia is the large scale production of electrolytic hydrogen, part of which is burnt in air to give the requisite nitrogen. The nitrogen-hydrogen mixture is then passed into steel cylinders containing coaxial annular chambers,<sup>5</sup> so that the walls of the vessel are protected from the hot hydrogen. The pressure employed is 300 atmospheres, and a special catalyst is claimed which functions in spite of relatively impure nitrogen and hydrogen. Mention has been made that 70 to 75 per cent. of the total costs of the Haber and Claude synthetic ammonia processes is the preparation of pure gases so that the catalyst will not be "poisoned." The catalytic material<sup>6</sup> of the Casale process is made by bringing iron into violent ebullition with oxygen under pressure in the presence of alkaline earth oxides. About 10 per cent. of the oxidation product is allowed to vaporise so as to remove impurities detrimental to the catalysis. A certain predetermined amount of ammonia is mixed with the mixture of nitrogen and hydrogen; the ammonia is liquefied by refrigeration and an amount equal to that formed removed, and the gases again subjected to catalysis.

A later patent of Casale<sup>7</sup> embodies the use of the oxygen obtained from the electrolysis of water. A gas approximating to the composition of water-gas is obtained by passing an oxygen-air mixture into a generator burning lignite or peat. This gas is then burnt in oxygen in a power generator, and the resulting gaseous mixture of hydrogen, nitrogen, and carbon dioxide is compressed by a multiple stage compressor varying from 100 to 1000 atmospheres. The carbon dioxide is removed by passing the compressed gases through a refrigerator cooled below  $30^{\circ}\text{C}$ . and is drawn off in the liquefied form. The last traces of carbon dioxide are removed by scrubbing with water, and the nitrogen-hydrogen mixture is enriched with electrolytic hydrogen to obtain the right proportions. Recirculation of the uncombined gases through the catalyst bombs occurs after removal of liquefied ammonia.<sup>8</sup> A successful technical plant on the Casale principle has been installed at Terni in

<sup>1</sup> Claude, *English Patents*, 174327 (1921), 175605 (1921); *J. Soc. Chem. Ind.*, 1922, 41 463A, 670A.

<sup>2</sup> Norsk Hydroelekt., *English Patent*, 205477 (1924).

<sup>3</sup> Claude, *English Patent*, 153254 (1922); *J. Soc. Chem. Ind.*, 1922, 41, 215A.

<sup>4</sup> Casale, *English Patents*, 148885 (1920), 176144 (1920), 185179 (1921), 194740 (1921), 193789 (1922), 200376 (1922), 197655 (1923), 221102 (1923), 221956 (1923); *United States Patents*, 1384428 (1921), 1408987 (1922), 1447123 (1923).

<sup>5</sup> Casale, *United States Patent*, 1478549 (1923).

<sup>6</sup> Casale, *English Patents*, 197199 (1922), 227491 (1923).

<sup>7</sup> Casale, *English Patent*, 233040 (1924).

<sup>8</sup> For diagrams of catalyst bombs, see p. 105.



Italy, where the great waterfalls provide ample power for the electrolytic hydrogen (and oxygen).

**Fausser Process.**<sup>1</sup>—The initial source of the nitrogen in the Fausser process is liquid air, and hydrogen of 99 per cent. purity is produced electrolytically. The special advantage of this process is that when used in conjunction with an ammonia oxidation plant, much nitrogen can be obtained from the residual gases after the oxidation to nitric acid and oxides of nitrogen. These gases, which contain relatively much nitrogen and little oxygen, are mixed with hydrogen and passed over platinum asbestos. The oxygen is removed as water, and practically pure nitrogen is now available for combination with hydrogen in the catalyst chamber. This latter takes the form of a bomb, and the nitrogen-hydrogen mixture at 300 atmospheres pressure is passed in. Preheating of the gases is effected by a system of heat interchangers which makes use of the heat of reaction, and the right temperature is secured finally by means of an electrically heated spiral. The heat of the gases from the catalyst chamber is used to volatilise ammonia from the solution obtained by absorbing the gas which has escaped liquefaction. The water serves as a lubricant for the compressors, and the ammonia liberated from the aqueous solution is obtained in the liquid form after cooling. The Fausser process offers a very economical method of nitrogen fixation, given an ample supply of water-power for producing electrolytic hydrogen, as a kilogram of nitrogen in the form of ammonia requires 17 K.W. hours direct current, and 19 K.W. hours if in the form of nitric acid.

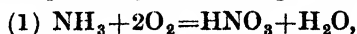
**Oxidation of Ammonia.**—The direct oxidation of ammonia to nitric acid has been known for a considerable time, as shown by the experiments of Milner, who, in 1788, passed a mixture of ammonia and air over heated manganese dioxide with the production of oxides of nitrogen. Apparently saltpetre was made on the large scale in France during the Napoleonic wars by Milner's method.<sup>2</sup>

Kuhlmann<sup>3</sup> in 1839 brought about a similar reaction by passing a mixture of ammonia and air over platinum sponge heated to 300° C. The well-known lecture experiment<sup>4</sup> consists in introducing a hot platinum spiral into a flask containing ammonia solution through which oxygen is passing, when a series of explosions occurs with the formation of red nitrous fumes.

Many other catalysts have been proposed from time to time, some of which have been patented; these include platinum in different forms, manganates, permanganates, chromates, bichromates, iron, iron oxides, plumbites, platinised glazed porcelain, ceria, and thoria.

In 1900<sup>5</sup> an exhaustive study was made of the necessary conditions for the oxidation of ammonia by means of platinum, and patents were taken out in 1902 for the production of nitric acid on the technical scale.

The final reaction is probably summed up in the equation



but actually in practice at least four steps have to be realised.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1923, 42, 835, 601A; A. Zambianchi, *Giorn. Chim. Ind. Appl.* 1923, 5, 171.

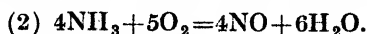
<sup>2</sup> Black, *Lectures on Chemistry*, 1803, pp. 245, 455.

<sup>3</sup> Kuhlmann, *Annalen*, 1839, 29, 280.

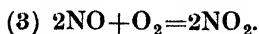
<sup>4</sup> First devised by Kraut, *ibid.*, 1865, 136, 69.

<sup>5</sup> Ostwald and Brauer, *English Patents*, 698, 8300 (1902), 7909 (1908).

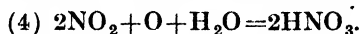
Thus the first product of oxidation is nitric oxide :



This nitric oxide is then converted into the dioxide by means of oxygen (air) :<sup>1</sup>



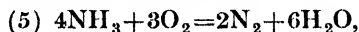
Thirdly, the conversion of nitrogen peroxide into nitric acid occurs under the combined action of oxygen (air) and water :



Finally, the dilute nitric acid thus produced has to be concentrated.

Ostwald's experiments were first conducted with ordinary smooth platinum and also the finely divided metal.

It was found that while smooth platinum favoured the reaction (1), the use of platinum black caused the oxidation of the ammonia to occur largely in the sense of the equation



although at the same time the oxidation, according to equation (1), was accelerated.

It was found, however, that on the technical scale platinum black was unsuitable—even in small amounts. Ordinary platinum, in the form of spirals or gauze, was found to be quite efficient, provided that correct conditions were used as regards volumes of ammonia and air, pressure and the temperature of the catalyst. The required oxygen is furnished by using 10 volumes of air to 1 volume of ammonia, and this mixture is passed at the rate of 1.5 metres per second through 1 to 2 cm. of contact substance maintained at 300° C. The nitric acid is condensed in vitreous receivers cooled by water, while uncondensed nitric acid vapours are passed into the absorption towers, where they meet nitric acid.

As with other processes, there are numerous modifications of the catalyst vessel—the so-called “converter.”

The original Ostwald type is used by the Nitrogen Products Company at Dagenham Dock. Crinkled platinum foil is used in an inner nickel tube surrounded by an outer iron tube. The initial heating of the catalyst by a hydrogen flame starts the reaction, and the heat evolved from the reaction serves to maintain the incoming gases at the right temperature (800° to 830° C.), so that once started no external heating is required.

The Frank-Caro converter uses a platinum gauze heated electrically, and this type is found to be very efficient, especially for supplying nitrogen oxides to the chambers in sulphuric acid manufacture. The Kaiser patent<sup>2</sup> was the first to utilise multiple super-imposed gauzes of platinum in close contact, and the preheating of the gases to 300°–400° C. This new feature is the basis of all modern developments in the oxidation converter. The Partington A1 Converter<sup>3</sup> makes use of a modified Frank-Caro type, and consists of a top and bottom cone of enamelled iron, containing a vertical double

<sup>1</sup> Various oxides of nitrogen may be produced at different temperatures (Andrussov, *Zeitsch. angew. Chem.*, 1926, 39, 321).

<sup>2</sup> Kaiser, *English Patents*, 20325 (1910), 24035 (1911); *German Patent*, 271517 (1914).

<sup>3</sup> Partington, *J. Soc. Chem. Ind.*, 1918, 37, 337R.

layer of platinum gauze with an exposed surface 6 inches by 4 inches, made with wire 0.0025 inch diameter and 80 mesh. The gaseous mixture is obtained by blowing air through pure 25 per cent. ammonia liquor, and the proportion of constituents is 7.5 volumes of air to 1 volume of ammonia, which is that required theoretically to give nitrogen trioxide,  $N_2O_3$ . The platinum gauze is heated externally to 650°–700° C. initially, after which the temperature is maintained by the heat

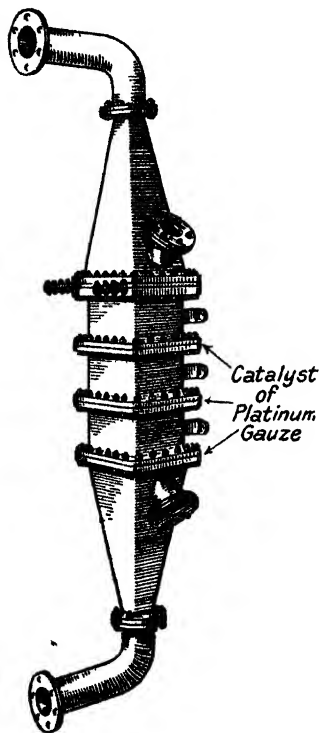
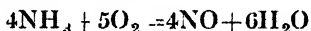


FIG. 25.—Ammonia oxidation converter.

of the reaction (220 Cals.); preheating of the gases to about 400°–600° C. improves the yield. The conversion efficiency is from 92 to 95 per cent., and the output is 1.5 tons of nitric acid per square foot of converter cross-section (2 square feet total gauze area) per twenty-four hours.

A converter of the above dimensions is capable of supplying a large chamber sulphuric acid plant with all the necessary oxides of nitrogen, thus completely dispensing with nitre pots. The above work by Partington was carried out for the Munitions Inventions Department, and an interesting feature was the separation of water from the oxidation product of the converter by rapid cooling. The equation expressing the reaction



shows that removal of steam will result in a considerable concentration of the nitric oxide, although of course the condensed steam will contain nitric acid which is worth concentrating or absorbing with alkali. The further oxidation of the oxides to nitric acid is brought about by addition of secondary air after the coolers.

Partington<sup>1</sup> has much further improved the efficiency of the above type of converter by the substitution of oxygen for air, whereby an almost quantitative conversion is obtained. Two gauzes in contact are used, and, in order to damp down the explosive mixture of ammonia and oxygen, steam is mixed with the gases, which are preheated to 500° C.<sup>2</sup> The correct mixture is obtained by volatilising ammonia liquor (sp. gr. 0.88) in sufficient oxygen, *i.e.* that required to completely oxidise the ammonia to nitric acid :



Direct cooling after conversion results in the production of a fairly concentrated acid, and absorption is dispensed with.

Partington has determined experimentally the various conversion

<sup>1</sup> Partington, *United States Patent*, 1378271 (1921).

<sup>2</sup> A high velocity may be obtained by the use of a flat, narrow reaction chamber. Cederberg, *English Patents*, 246889 (1926), 244134 (1927).

efficiencies obtained by various types of converters, and his results are tabulated below : <sup>1</sup>

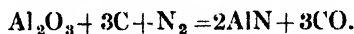
Type of Converter.	Catalyst.	Method of Heating.	Conversion Efficiency	Output kgm HNO <sub>3</sub> per Gram Pt per 24 Hours.
Ostwald . .	Platinum foil	Regenerative	Per cent. 90-95	1.7-2
Frank-Caro .	Single platinum gauze	Electrical	90-93	11
Kaiser . .	4 superposed platinum gauzes	Preheating of gases	95	12
Partington .	2 platinum gauzes slightly separated	Electrical or pre-heating of gases	95	16
Partington (with oxygen)	2 platinum gauzes in contact	Gases and steam preheated to 500° 600° C.	98 99	21

**Formation of Nitrides.**—Many attempts have been made to fix atmospheric nitrogen in the form of metallic nitrides, e.g. AlN, Mg<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>N<sub>2</sub>, etc., by the direct combination of the elements at a high temperature. The production of ammonia is then effected by the decomposition of these compounds by water or steam :



*Serppek Process.* When aluminium is heated in an atmosphere of nitrogen the metal increases in weight, and when the product is fused with potash, ammonia is evolved.<sup>2</sup> Aluminium also forms a nitride when heated to 700° C. in an atmosphere of ammonia.<sup>3</sup> These observations are the basis of the Serppek<sup>4</sup> process of fixing atmospheric nitrogen gas, which was worked technically for a time in the Savoy.

Finely divided alumina, (Al<sub>2</sub>O<sub>3</sub>), heated by furnace gases, passes down an inclined tube, is mixed with powdered coke, and passes through a zone electrically heated to 1800° C. It there meets a current of nitrogen derived from the combustion of producer gas, with the formation of aluminium nitride and carbon monoxide :



The carbon monoxide, mixed with more air, is burnt to heat the first tube through which the cold alumina is introduced. The aluminium nitride readily hydrolyses—especially with water under pressure, and the hydroxide produced can be used for the production of metallic aluminium.

Originally the mixture of bauxite and carbon was heated in contact with nitrogen in rotating furnaces, but later Serppek<sup>5</sup> used a short

<sup>1</sup> Adapted from *A Dictionary of Applied Chemistry*, by Thorpe, Vol. iv (Longmans, 1922).

<sup>2</sup> Briegleb and Geuther, *Annalen*, 1862, 123, 38.

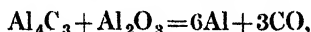
<sup>3</sup> White and Kirschbaum, *J. Amer. Chem. Soc.*, 1906, 28, 1343.

<sup>4</sup> *English Patent*, 13086 (1919).

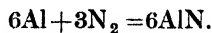
<sup>5</sup> Serppek, *Zeitsch. Komprimierte flüss. Gase*, 1914, 16, 55.

chamber in which the mixture, preheated to  $1250^{\circ}$ – $1300^{\circ}$  C., meets the current of nitrogen.

With regard to the mechanism of the reactions occurring during the process, Serpck assumed that aluminium carbide,  $\text{Al}_4\text{C}_3$ , was first formed, which reduced the remaining oxide to the metal,



and the aluminium then combined directly with nitrogen to form the nitride,

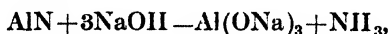


The presence of certain impurities, such as oxides of iron and copper, acts catalytically, so that bauxite, which contains iron oxide, is a good raw material. The Badische Company<sup>1</sup> accelerate the reaction by mixing with the alumina and coal 5 to 6 per cent. of oxides of silicon, titanium, vanadium, etc., which themselves form stable nitrides, from which the oxides can be recovered and used again.

The presence of such catalytic materials also enables the reaction to proceed at a lower temperature than would be possible with the pure alumina. The formation of aluminium nitride begins at  $1100^{\circ}$  C., and the yield increases with temperature to a maximum at  $1800^{\circ}$  to  $1850^{\circ}$  C. Above  $1900^{\circ}$  C., however, smaller yields are obtained owing to the dissociation of aluminium nitride into its constituents, and at  $2000^{\circ}$  C. no nitride was formed at all.

Although other metals, such as lithium, magnesium, calcium, etc., form nitrides readily, they are too expensive for technical use owing to the difficulty of recovering the metal from the hydroxide produced after hydrolysis. Hence aluminium is really the only suitable metal which has been the subject of technical investigation.

In actual practice the hydrolysis of the aluminium nitride is brought about by means of alkali,



and the sodium aluminate can be either converted by the Baeyer process<sup>2</sup> into pure alumina, which is again used for making the nitride, or the metal. In the Serpck process potassium hydroxide solution was used in insufficient amount for the formation of the aluminate, so that the alumina remaining served to form fresh quantities of the nitride.

**Formation of Alkali Cyanides.**<sup>3</sup> The synthesis of potassium cyanide by heating a mixture of potassium carbonate and carbon to a high temperature in an atmosphere of nitrogen was first discovered by Scheele in 1784. Bunsen and Playfair<sup>4</sup> in 1848 investigated the reaction between atmospheric nitrogen, potassium and carbon compounds, following the discovery of Dawes in 1885 that potassium cyanide was a product of the blast furnace. Incidentally it may be mentioned that it<sup>5</sup> has recently been suggested that about 1 per cent. of the nitrogen of the air blast could be recovered as cyanide without interfering with the production of iron in the blast furnace.

<sup>1</sup> Badische Company, *German Patent*, 243839 (1912).

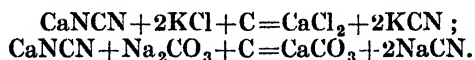
<sup>2</sup> This series, Vol. IV.

<sup>3</sup> See also under Cyanides, this Series, Vol. V.

<sup>4</sup> Bunsen and Playfair, *B.A. Report*, 1845.

<sup>5</sup> Franchot, *J. Ind. Eng. Chem.*, 1924, 16, 235.

Many attempts have been made to manufacture potassium cyanide from the carbonate, carbon, and nitrogen, but the greatest drawback is the deterioration of the furnace by the materials used at the high temperature required. It has been found possible, however, to prepare technically pure potassium cyanide (and sodium cyanide) indirectly by fusing crude calcium cyanamide,  $\text{CaNCN}$ , with the corresponding chloride or carbonate:



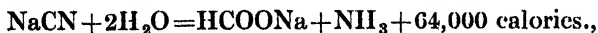
*Bucher Process.*—Interest in the original cyanide synthesis was revived by the exhaustive investigation of J. E. Bucher<sup>1</sup> into the production of cyanides as a method of nitrogen fixation, and various patents were taken out during the years 1914 to 1917. Essentially the process consists in the reaction between sodium carbonate, carbon, and nitrogen at a high temperature in the presence of finely divided iron which acts catalytically:



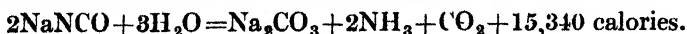
As regards raw materials, sodium carbonate in the commercial form of soda ash is used; coke, either metallurgical, petroleum, or pitch, may be employed with technical success, the latter form being practically ashless, which obviates the periodic removal of material; with regard to the nitrogen, it seems that at present there is insufficient data to determine whether pure nitrogen or producer gas has any special advantages.

The finely divided mixture of soda ash, coke, and iron is made up into briquettes, which are fed into externally heated vertical retorts heated to  $900^\circ\text{--}950^\circ \text{C.}$ , and nitrogen passed into the retorts under slight pressure. The reaction is of a complex nature, but probably the iron assists in the reduction of sodium carbonate to metallic sodium. After four hours' heating the final product yielded cyanide to the extent of a 50 per cent. conversion of sodium carbonate. Bucher proposed lixiviation of the cyanised material with water to extract the cyanide as such, but the chief disadvantage is the solution of unchanged sodium carbonate. If sodium cyanide is required, the process worked for some time by the Nitrogen Products Company would seem to be advantageous, whereby liquid ammonia was used to leach out the cyanide, upon which it exerted a selective solvent action.

The original idea of Bucher was to fix nitrogen as ammonia or ammonia derivatives, chiefly by hydrolysis of the cyanide. Thus, at relatively low temperatures the production of ammonia and sodium formate occurs,



and any cyanate which has been formed by oxidation is converted into ammonia, carbon dioxide, and sodium carbonate:



At higher temperatures ( $400^\circ$  to  $500^\circ \text{C.}$ ) the hydrolysis of the cyanide occurs, with the formation of sodium formate and ammonia as

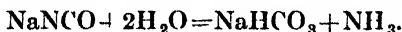
<sup>1</sup> J. E. Bucher, *J. Ind. Eng. Chem.* 1917, 9, 233.

before, but the formate is broken down at that temperature into the carbonate, hydrogen, and carbon monoxide :



The sodium carbonate produced could be returned to the cyanising retorts.

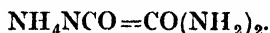
Bucher suggested that further developments of this process might consist of heating the cyanide in air, whereby oxygen would be removed from the latter to form cyanate, and the nitrogen could be used for the cyanising furnace. If, then, one-half of the cyanate were heated with water, production of ammonia and sodium bicarbonate would occur :



The other half of the cyanate would react with this ammonia and carbon dioxide (produced by burning the carbon monoxide from the cyanising furnace) in the presence of water to form ammonium cyanate :



Intramolecular change converts ammonium cyanate into urea :



The possibility of a cheap large scale production of urea is attractive, as modern research indicates that this substance is ideal for fertilising purposes.

An interesting modification of the Bucher process is the subject of patents by C. B. Jacobs<sup>1</sup> of the E. I. du Pont de Nemours Powder Company. Instead of briquetting, the addition of 5 per cent. sodium fluoride or chloride is made, which acts as a flux. Further, a reactive form of carbon is used which is obtained by incinerating black liquor at 200° to 300° C. This latter substance is produced from the digestion of wood and other cellulosic materials with caustic soda.

The composition of a typical charge is :

Sodium carbonate . . .	40 per cent.
Carbon . . . . .	40 „
Ferric oxide . . . . .	15 „
Sodium fluoride . . . . .	5 „

It is claimed that at 925° to 950° C. a 95 to 98 per cent. conversion of sodium carbonate is obtained in two hours.

After all volatile matter has been expelled by heating, nitrogen in the form of producer gas is passed in under a pressure of 20 pounds above atmospheric, and this is continued until no more carbon monoxide is evolved. This gas is utilised by mixing with producer gas and burning under the retorts.

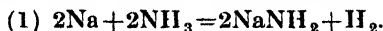
Extraction of the mass with water yields a 96 to 98 per cent. pure cyanide after crystallisation. The above description of the modified Bucher process is given, because it would appear that the original process was not economical enough to fulfil expectations. According to Guernsey and Sherman,<sup>2</sup> the mechanism of the reaction is the reduction

<sup>1</sup> Jacobs, *English Patent*, 200902 (1922); *U.S. Patent*, 1481373-4 (1924).

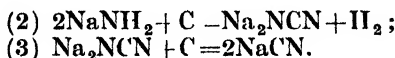
<sup>2</sup> Guernsey and Sherman, *J. Amer. Chem. Soc.*, 1925, 47, 1932; see also Guernsey, Yeo, Braham, and Sherman, *J. Ind. Eng. Chem.*, 1926, 18, 243.

of sodium carbonate to metallic sodium, which then forms sodium carbide, and this latter compound reacts with nitrogen to form the cyanide, assisted by the iron as catalyst.

Reference should be made here to the fact that at present the only large scale production of sodium cyanide is the Castner-Roessler process, the sole rights of which are owned by the Deutsche Gold und Silber Scheidenanstalt. In this process metallic sodium and ammonia are caused to react at  $300^{\circ}$  to  $400^{\circ}$  C., with the formation of sodamide :

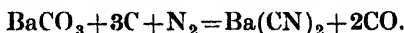


The molten sodamide is then brought into contact with red-hot charcoal, the final product being sodium cyanide, while sodium cyanamide is formed intermediately :

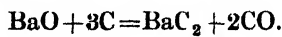


It has already been mentioned that the sodium cyanide may be used as a potential source of ammonia by hydrolysis with steam. It must not be overlooked, however, that sodium cyanide is being used largely in the metallurgical industry—especially in gold extraction, and also that it has a limited use as an insecticide.

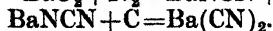
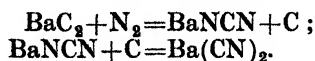
*Barium Cyanide.*—In the description of the cyanamide process (*infra*) reference is made to the simultaneous formation of calcium and barium cyanides and cyanamides by heating the carbonates and carbon in nitrogen. Many attempts have been made to manufacture barium cyanide as a source of ammonia, but at the present time it would seem that this process has not developed into a commercial success. There are two lines along which investigations have been made : the first a single-stage process which resembles the Bucher process for sodium cyanide, and the second a two-stage process closely allied to the manufacture of cyanamide. The first process consists in briquetting a mixture of barium carbonate and carbon (pitch or tar) and passing nitrogen over the mixture heated to  $1000^{\circ}$ – $1400^{\circ}$  C. :



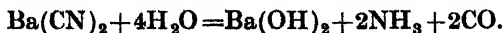
In the second process, the first stage is the production of barium carbide by heating barium oxide and carbon in the electric furnace :



The second stage is the formation of barium cyanide by treating the carbide with nitrogen at about  $1000^{\circ}$  C. It is probable that barium cyanamide is formed as an intermediate product :



The barium cyanide from either process may be treated with steam, when hydrolysis occurs, with the formation of ammonia and barium hydroxide :



Theoretically, the barium hydroxide can be utilised again for the production of cyanide, but considerable practical difficulties are

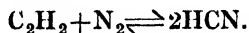


encountered. The high initial cost of the barium carbonate (and hydroxide) compared with that of calcium carbonate is a great disadvantage in making a comparison of the cyanide and cyanamide processes. One of the great drawbacks of the barium cyanide process is the corrosive action of the molten cyanide upon the retorts owing to the high temperature employed. Recently, Askenasy<sup>1</sup> has suggested that this may be obviated to a large extent by using a carbon of low ash content, such as petroleum coke or soot. This should be preheated to a temperature above that employed for its production, and should also be treated with oxygen or chlorine.

Another method<sup>2</sup> for obtaining an intimate mixture of barium oxide and carbon is by decomposing methane with hot barium oxide, the particles of which become coated with carbon particles. The hydrogen from the methane is utilised for providing heat for the furnace, and also for the reaction of the mixture of barium oxide and carbon with atmospheric nitrogen as cyanide.

*Hydrocyanic Acid.* It would seem desirable to indicate processes which have been proposed from time to time to fix atmospheric nitrogen in the form of hydrogen cyanide. So far, however, there is no large scale process of any importance which makes practical use of the synthesis of hydrocyanic acid.

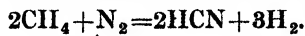
Berthelot<sup>3</sup> discovered that acetylene and nitrogen combined together with the aid of electric sparks to form hydrogen cyanide, and that the reaction was reversible :



Later, Dewar<sup>4</sup> showed that a mixture of hydrogen and nitrogen when passed through a carbon tube heated externally resulted in the production of hydrocyanic acid.

Hoyermann<sup>5</sup> repeated Berthelot's synthesis by passing a mixture of 2 volumes of nitrogen and 1 volume of acetylene through a carbon arc, and obtained a 60 to 70 per cent. conversion of acetylene into hydrocyanic acid.

Gruskiewicz<sup>6</sup> found that hydrogen cyanide was produced when sparks were passed through a mixture of carbon monoxide, nitrogen, and hydrogen. Lipinsky<sup>7</sup> considered that the carbon monoxide was first reduced to methane, on account of his experiments with a mixture of methane (from natural gas), nitrogen, and hydrogen :



Lipinsky's method was tried on the technical scale at Neuhausen in Switzerland in 1914, when a quantitative conversion of methane into hydrocyanic acid was claimed. The mixture consisted of 20 per cent. methane, 70 per cent. nitrogen, and 10 per cent. hydrogen, which was passed through an arc between platinum electrodes from a 2200-volt alternating current supply. The hydrogen and excess of nitrogen were

<sup>1</sup> Askenasy, *German Patent*, 382041 (1922); *Metzger, J. Soc. Chem. Ind.*, 1924, 43, 94B.

<sup>2</sup> H. Lentz, *German Patent*, 361864 (1920); *J. Soc. Chem. Ind.*, 1924, 43, 133B.

<sup>3</sup> Berthelot, *Compt. rend.*, 1868, 67, 1141.

<sup>4</sup> Dewar, *Proc. Roy. Soc.*, 1879, 29, 188; 1880, 30, 85.

<sup>5</sup> Hoyermann, *Chem. Zeit.*, 1902, 26, 70.

<sup>6</sup> Gruskiewicz, *Zeitsch. Elektrochem.*, 1903, 9, 83.

<sup>7</sup> Lipinsky, *ibid.*, 1911, 17, 761.

employed merely as a diluent, and it is stated that 30 grams of hydrocyanic acid per K.W. hour were obtained.<sup>1</sup>

A somewhat different method of causing gaseous carbon and nitrogen compounds to combine was used by Beindl,<sup>2</sup> who employed a catalyst material consisting of a metal, its oxide and nitride.

The Chemischerfabrik Griesheim Elektron propose the passing of a nitrogen-hydrogen mixture over coke in an electric furnace; while a more recent process by the Norsk Hydroelektrisk Kvaestofaktieselskab<sup>3</sup> makes use of a blown-arc furnace of the Birkeland-Eyde type, through which a mixture of nitrogen, hydrogen, and a hydrocarbon is passed.

The subsequent treatment of the hydrocyanic acid is either for the production of cyanides by absorption with alkalis, oxidation by burning in air to nitric oxide for conversion into nitric acid, or hydrolysis with steam at a high temperature with the formation of ammonia.

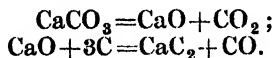
**Cyanamide.**—Some of the earliest experiments for the preparation of cyanamide compounds were those of Marguerette and Sourdeval<sup>4</sup> in 1860 in connection with the preparation of barium cyanide,  $\text{Ba}(\text{CN})_2$ , by heating a mixture of carbon and barium carbonate in air. The first technical application was used by the Badische Company<sup>5</sup> in 1896, who obtained a mixture of the cyanide and cyanamide,  $\text{BaNCN}$ , by heating the mixture at  $1500^\circ \text{C}$ . in an atmosphere of nitrogen.

The use of barium carbide instead of the mixture of carbonate and carbon was introduced by Frank and Caro<sup>6</sup> in 1898, who found that if the carbide is used in large lumps, barium cyanide is almost exclusively produced, whereas a yield of 70 per cent. of barium cyanamide is obtained if small granules of carbide are used.

The technical manufacture of alkali cyanides for gold extraction by fusion of the mixture of cyanide and cyanamide with alkali chlorides was made use of by the Gold und Silber Scheidenanstalt of Frankfurt.<sup>7</sup>

**Calcium Cyanamide.**—The substitution of calcium carbide for the barium compound by Pfleger, Rothe, and Freudenberg caused the process to become more economical, and Frank and Caro<sup>8</sup> patented the process during the years 1895–98. The real impetus given to the technical production of calcium cyanamide was the discovery in 1901 that this substance could be used directly as a fertiliser.

The essential materials for the manufacture of calcium cyanamide are limestone, carbon, and nitrogen. The production of calcium carbide is effected by first burning the limestone ( $\text{CaCO}_3$ ) to lime ( $\text{CaO}$ ), and then fusing of the lime with carbon (anthracite coal, or coke) in an electric furnace:<sup>9</sup>



<sup>1</sup> H. Phillips, *Chem. Met. Eng.*, 1920, 22, 213.

<sup>2</sup> Beindl, *English Patent*, 10321 (1915).

<sup>3</sup> Norsk Hydroelektr., *English Patent*, 235181 (1925).

<sup>4</sup> Claude, *English Patents*, 1027, 1172 (1860); Marguerette and Sourdeval, *Compt. rend.*, 1860, 50, 1100.

<sup>5</sup> Badische Company, *German Patents*, 190955 (1907), 197394 (1908).

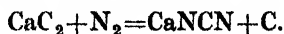
<sup>6</sup> Frank and Caro, *German Patents*, 108971 (1900), 116087 (1900), 116088 (1900); *English Patent*, 25475 (1898). See also Erlwein, *Zeitsch. angew. Chem.*, 1903, 16, 533.

<sup>7</sup> Frank and Caro, *German Patent*, 212706 (1909).

<sup>8</sup> Frank and Caro, *Zeitsch. angew. Chem.*, 1906, 19, 835; 1909, 22, 1178.

<sup>9</sup> See this series, Vol. III., Part I.

The direct fixation of nitrogen is brought about by heating the powdered calcium carbide in an atmosphere of nitrogen :

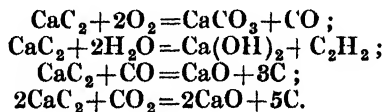


As in other fixation processes, one of the most important points with the cyanamide process is the purity of the reacting substances. Thus the initial raw material limestone—must contain about 97 per cent. of calcium carbonate with relatively small amounts of magnesium carbonate and oxides of aluminium, otherwise the fluidity of the carbide is decreased. Silicon and iron tend to produce ferrosilicon, which gives furnace trouble and difficulty in grinding the carbide. Phosphorus in the form of calcium phosphate is very deleterious even in small quantities, as calcium phosphide is produced in the furnace, which with moisture produces phosphine, and is especially objectionable if the cyanamide is hydrolysed to ammonia which is subsequently to be oxidised to nitric acid.

*Formation of Calcium Cyanamide.*—Calcium carbide is finely crushed and heated in contact with nitrogen under slight pressure, when absorption begins at 700° to 800° C. and becomes rapid at 1000° C. The equation



shows the reaction to be exothermic, and once started, the heat of formation is sufficient to carry the process to completion. It is obvious that an abundant supply of nitrogen is necessary, and this is generally obtained from the liquefaction of air by either the Linde or Claude rectification plant, although in part of the Niagara works nitrogen is obtained from air by the copper-cupric-oxide reaction. The absence of oxygen, moisture, carbon monoxide, and carbon dioxide is very desirable, otherwise various by-reactions take place, decreasing the yield of cyanamide :



Moissan<sup>1</sup> found that pure calcium carbide and nitrogen would not react at 1200° C., but Rothe<sup>2</sup> discovered that nitrification proceeded rapidly if the crude carbide was used. It would appear that some form of catalytic material was necessary for the reaction, and Polzenius<sup>3</sup> patented the use of calcium chloride in 1901. Thus, whereas with no calcium chloride there was less than 1 per cent. of nitrogen absorbed in twelve to fourteen hours at 730° C., yet under the same conditions with 10 per cent. of calcium chloride 18 per cent. of nitrogen was absorbed (as against 22 per cent. theoretical absorption).

The disadvantage in the use of calcium chloride, however, is the deliquescent nature of the final product. The action of water is to generate acetylene from the residual carbide and to form dicyanodiamide,  $(\text{CN.NH}_2)_2$ , from the cyanamide, which is deleterious when the cyanamide is to be used for fertiliser purposes. Dicyanodiamide is

<sup>1</sup> Moissan, *Compt. rend.*, 1894, 118, 501.

<sup>2</sup> Rothe, *English Patent*, 25476 (1898). See also *Zeitsch. angew. Chem.*, 1903, 16, 658.

<sup>3</sup> Polzenius, *German Patent*, 163320 (1901).

toxic to plant life, partly because it inhibits the action of nitrifying bacteria.

In 1906 the use of calcium fluoride, ( $\text{CaF}_2$ ), was suggested in the form of crushed fluor-spar as a catalyst for carbide nitrification, and apparently most modern works now employ this substance.

The ovens used in the process of nitrification are either of the continuous or discontinuous type. The former type, as worked at Knapsack in Germany and Marignac in France, consists of metal boxes filled with carbide which are pushed through a long tunnel filled with nitrogen and heated either electrically or by means of producer gas. The Carlson Company in Sweden use cylindrical ovens, fitted with shelves, filled with nitrogen and heated at the top by arcs to a temperature of  $950^\circ \text{C}$ . The carbide is worked downwards by a mechanical scraper from shelf to shelf, and the cyanamide is discharged at the bottom of the oven after a period of two hours. The discontinuous type of oven is of the more common type, and may be externally fired or electrically heated. The electric furnace, such as is used at Odda in Norway, consists of a metallic cylindrical oven heavily lined with refractory material, so that the internal dimensions are about 5 feet by 3 feet. Nitrogen is forced in at the bottom, and the calcium carbide in a heavy container is heated by means of a carbon pencil passing through the centre, which carries a single-phase current of 100 volts and 200 to 250 amperes. After a few hours the current is switched off, as the heat of the reaction is then sufficient to carry the process to completion. Nitrification proceeds from the core outwards, the temperature in the furnace being about  $1100^\circ \text{C}$ . About 85 per cent. only of calcium carbide undergoes nitrification, and the rest is destroyed in some unexplained way during the reaction, as there is only 1 to 2 per cent. of carbide in the crude cyanamide. Generally speaking, the nitrogen content of the cyanamide varies between 19 and 20 per cent. according to furnace practice, quality of raw materials, etc., in different countries. A typical analysis of cyanamide produced at Muscle Shoals in the United States is given : <sup>1</sup>

	Per cent.
Calcium cyanamide . . . . .	61.2
.. oxide . . . . .	20.0
.. carbide . . . . .	1.5
.. sulphide . . . . .	0.2
.. phosphide . . . . .	0.04
Free carbon . . . . .	12.5
Silica . . . . .	2.4
Iron and aluminium oxides . . . . .	1.8
Magnesium oxide . . . . .	0.2

The crude product, which sinters to a solid greyish-black cake, is then crushed and milled. The small amount of residual carbide is very objectionable, and the only efficient way to remove same is to spray with water, when acetylene is generated. Insufficient water must be used than will form dicyanodiamide, and modern practice favours the use of a water-and-oil spray, especially if the cyanamide is to be used as a fertiliser. The water, to the extent of 6 to 7 per cent. of the weight of cyanamide, decomposes the carbide and hydrates the free

<sup>1</sup> Report on Fixation and Utilisation of Nitrogen, U.S. War Department, 1922.  
VOL. VI. : 1.

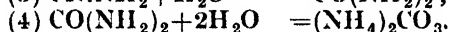
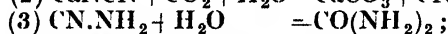
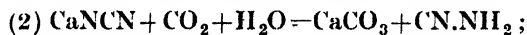
lime, but does not remove dustiness, which is effected by a spray of mineral oil (3 to 4 per cent. of the weight of cyanamide).

*Uses of Cyanamide.*—1. *Fertiliser.*—The crude calcium cyanamide, known as “nitrolim,” “lime-nitrogen,” “kalkstickstoff,” etc., has the great advantage of cheapness. On the other hand, there is considerable difficulty in its storage owing to the action of atmospheric moisture and carbon dioxide, which results in the formation of dicyanodiamide. As has already been mentioned, this latter substance is not only directly toxic to plant life, but it also prevents the action of nitrification bacteria in the soil. Hence treatment and storage of cyanamide is a matter of first-rate importance; the water-and-oil treatment described above is very necessary, and when stored in double burlap bags it can be kept for six to twelve months without deterioration.

The actual mode of decomposition of calcium cyanamide in the soil is apparently very complex, the main reaction being the hydrolysis of ammonia:



Another series of reactions, however, occurs whereby free cyanamide,  $\text{CN.NH}_2$ , urea, and ammonium carbonate are formed successively:



In each case the final product ammonia readily undergoes conversion into nitrate by means of bacterial action.

Attempts have been made to use cyanamide in various mixed fertilisers, but care has to be taken as regards the other constituents. Thus it cannot be used with acid phosphate owing to the reversion of this substance, and further, the formation of toxic dicyanodiamide. It seems feasible, however, to mix it with basic slag or superphosphate, or with a calcined phosphate containing a high percentage of citric acid soluble phosphate.

2. *Production of Ammonia from Cyanamide.*—One of the most attractive features of the cyanamide process of nitrogen fixation is the ready conversion of the cyanamide into ammonia by hydrolysis with water. The final reaction is shown in equation (1) above.

The first patent for this process was that of Frank<sup>1</sup> in 1900, and since that time the production of ammonia from cyanamide has been in commercial operation in many countries. A detailed description of the plant is given by Landis<sup>2</sup> with reference to the continuous production of ammonia by the American Cyanamide Company. In essence the process consists in treating cyanamide in an autoclave with alkali and steam under pressure, and once the action is started, sufficient heat is generated from the reaction to liberate completely practically all the ammonia.

The autoclaves are cylindrical in shape, about 21 feet in height and 6 feet in diameter, and are made of steel capable of withstanding a pressure of 300 lb. to the square inch. Filtrate liquor (19,000 lb.) from a previous operation is introduced, then sufficient soda ash to give an alkalinity of about 3 per cent. sodium hydroxide. About 9000 lb.

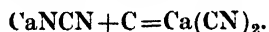
<sup>1</sup> Frank, *German Patent*, 134289 (1900); *U.S. Patent*, 776134 (1904).

<sup>2</sup> Landis, *Met. Chem. Eng.*, 1916, 14, 87.

of cyanamide are then introduced, and the charge well stirred, to decompose carbide and phosphide of calcium with the evolution of ammonia. Steam is then forced in at the bottom of the autoclave until the reaction begins, when about 90 per cent. of nitrogen is converted into ammonia, which is discharged with large volumes of steam into condensers. A further quantity of ammonia is obtained by forcing steam in again under a pressure of 120 lb. for two hours. The total conversion of nitrogen into ammonia is about 97 to 98 per cent., and, as the gas is practically pure, it can be utilised directly either for the preparation of ammonium salts or for oxidation to nitric acid.

The disposal of the autoclave sludge (after filtration) is one of the difficulties of the process, as although a number of proposals have been made, yet so far it would seem that a successful solution of the problem has yet to be found.

3. *Cyanides*.—The production of cyanides from cyanamide (p. 224) was the subject of much investigation after the work of Frank and Caro in 1900. The American Cyanamide Company<sup>1</sup> seem to be the first who erected a plant for the technical manufacture of calcium cyanide from calcium cyanamide in 1916. The process consists in heating a mixture of calcium cyanamide, carbon, and sodium chloride in an electric furnace to a temperature of 1300° C. and then rapidly cooling the molten product to prevent the reverse reaction taking place :

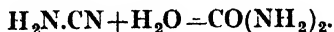


The sodium chloride apparently merely acts as a flux, although it is possible that the reaction is not as simple as indicated by the above equation.

The product, of course, is a very impure substance, the cyanide content of which varies between 35 and 50 per cent. equivalent of sodium cyanide. Successful application of this crude cyanide, however, has been made both for gold and silver metallurgy, and also for the production of hydrocyanic acid for fumigation purposes.

4. *Urea*.—At present urea has only a limited application for such things as medicinal preparations, synthetic glasses or resins, and celluloid products, but its high nitrogen content (46 per cent.) and freedom from any deleterious substances indicate that it would make an ideal fertiliser. Any process, therefore, which could be economically worked for large scale production of urea would allow an extensive use of this substance as plant food.

The reactions necessary to convert cyanamide into urea consist in extracting the crude substance with water, filtering the solution and adding excess of sulphuric acid. In this way all the calcium is removed as sulphate, and, on heating the solution, the free cyanamide,  $\text{H}_2\text{CN}_2$ , is hydrolysed to urea :



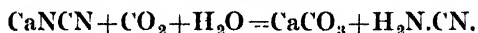
The excess of sulphuric acid is removed as calcium sulphate, and it is the cost of the sulphuric acid which constitutes the chief disadvantage in the process, as it is all lost in the form of the calcium salt.

The Lidholm process<sup>2</sup> for the manufacture of urea is now being worked by the Union Carbide Company at Niagara, and is a more

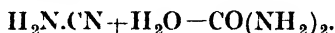
<sup>1</sup> Landis, *Met. Chem. Eng.*, 1920, 22, 265.

<sup>2</sup> Lidholm, *J. Chem. Met. Eng.*, 1925, 32, 791.

economical process. Calcium cyanamide is suspended in water and carbon dioxide passed in, which removes the calcium as carbonate and at the same time liberates free cyanamide :



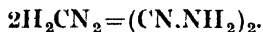
The hydrolysis of the cyanamide into urea is brought about by means of dilute sulphuric acid, and, owing to the extreme chemical activity of the cyanamide, this second stage immediately follows the liberation of the cyanamide :



The sulphuric acid is removed quantitatively by the addition of calcium carbonate, and the filtrate is evaporated in vacuum pans to a syrup which is practically molten urea, with a very small quantity of water. A "spheroidising" process consists in forming minute droplets by means of a blast of cold air on the molten product, which solidify as they fall through the air, producing a glazed surface which does not cake with water. The final product contains over 44 per cent. nitrogen, (pure urea contains 46.6 per cent.), of which 41 per cent. is in the form of urea, 1 per cent. in ammonium compounds, 1.5 per cent. in guanyl urea (which can slowly be utilised by plants), and a fractional percentage of dicyanodiamide.

5. *Free Cyanamide.* This compound can be obtained by extraction of the crude calcium salt with water, exactly neutralising the solution of calcium acid cyanamide,  $\text{Ca}(\text{HCN})_2$ , with sulphuric acid, and evaporating the filtrate at  $75^\circ \text{C}$ . If a higher temperature is reached, then an appreciable amount of urea is formed owing to hydrolysis.

6. *Dicyanodiamide.*—Free cyanamide readily polymerises to dicyanodiamide, and, after extracting with water as above, only half the sulphuric acid is added, so that only one-half of cyanamide is in the free form. The temperature is raised to  $75^\circ \text{C}$ ., and the remainder of the sulphuric acid gradually added so that polymerisation and liberation of the free cyanamide keep pace with each other :



7. *Guanidine.*—Various salts of guanidine are prepared by treating a solution of free cyanamide and the corresponding ammonium salt in an autoclave at  $155^\circ \text{C}$ .

**Survey of the Nitrogen Fixation Problem.**—*British Synthetic Ammonia.*—Up to the publication of this volume, by far the greatest proportion of the world's supplies of synthetic nitrogen compounds had been obtained by the combination of nitrogen and hydrogen.

Towards the end of the Great European War, the British Government had taken some steps to ensure supplies of fixed nitrogen within the national boundaries, and had begun some buildings on the chosen site at Billingham. The production of synthetic ammonia is distinguished by low-power costs. To combine 1 ton of nitrogen requires 8.4 K.W.Y. by the arc process, 2.0 K.W.Y. by the cyanamide process, and only 0.4 K.W.Y. by the ammonia process. Since electric power is not cheap in Great Britain, the arc process is out of the question. The cyanamide process (see p. 224) also requires power for the electrothermic production of calcium carbide. The ammonia process requires

pure hydrogen and nitrogen, obtained by the methods described on p. 210, and is very conveniently worked in conjunction with electrolytic and ammonia-soda-alkali processes. Thus the Government were well advised in 1920 to dispose of the site and information to "Synthetic Ammonia and Nitrates, Ltd.," a subsidiary company formed by Brunner, Mond & Co. A research staff was set to work out a modified Haber process, and plant was erected which, by the spring of 1925, was producing 30 tons of ammonia per day. This was soon increased to 50 tons, and it was expected that shortly the figure would approximate to 200 tons per day. This was the first industrial plant outside Germany to work at the low pressures of the Haber method, and at the present time England is the second largest synthetic ammonia-producing country in the world. The United Alkali Company has installed a full-scale plant for the manufacture of nitric acid by the oxidation of ammonia.

Germany, as would be expected, still maintains her position as being the largest producer of synthetic ammonia. In America much investigation has been carried out by the Fixed Nitrogen Research Laboratory of the United States Department of Agriculture. An enormous plant was erected at Muscle Shoals in 1919 for the manufacture of calcium carbide, from which ammonia and nitric acid were to be produced. Its capabilities were stated to be 40,000 tons of nitrogen per year, but it has never worked for full production, and it was put up for sale by private negotiation. A number of companies are engaged in the manufacture of cyanamide-ammonia by both the Claude and Casale processes, and also of cyanides by the Bucher process. The arc process is being developed by the American Nitrogen Products Company. France is extending the production of synthetic ammonia, and the Haber, Claude, and Casale processes are well in use. The Government plant at Toulouse, operated on the Casale principle, will have a capacity of 56,000 tons of ammonia per annum.

In Italy, both the Casale and Fauser processes are in operation, and the estimated output for 1926 is 42,000 tons of fixed nitrogen.

Spain is developing synthetic ammonia production on the Claude and Casale principles, and an ultimate output of 25,000 tons per annum is anticipated.

In Belgium, works are in the course of erection which will have an annual output of 10,000 tons of ammonia by the Casale process.

Thus it will be seen that the fundamental importance of artificial nitrogen fixation is being recognised by most countries. The following table<sup>1</sup> shows the estimated world production of nitrogen for the year ended 1st May 1925. The figures are expressed in tons of nitrogen (2240 lb.) :—

By-product ammonium sulphate	.	.	290,300 tons.
Synthetic	"	"	254,800 "
Cyanamide	.	.	115,000 "
Nitrate of lime	.	.	25,000 "
Other forms of synthetic nitrogen	.	.	60,000 "
Chilian nitrate of soda	.	.	363,000 "
Total	.	.	1,108,100 tons.

<sup>1</sup> *Gas World*, 83, 591, 1925.



*The Use of Combined Nitrogen in Agriculture and a Comparison of various Fertilisers.*—It is hardly an exaggeration to say that the greatest of all services rendered to humanity by chemistry is the ensurement of a practically inexhaustible supply of the most essential and at the same time the most perishable of plant fertilisers. The result should be that, given Governments with a proper appreciation of applied science and with a genuine aversion to war, the food-producing areas of the world should for all time be able to furnish their full quota of their different products.

The following striking examples<sup>1</sup> give some idea of the value of combined nitrogen in agriculture :—

One hundredweight of sodium nitrate or ammonium sulphate, or one and a half hundredweights of nitrolim applied to one acre of soil, increases the yield of potatoes by 1 ton, the yield of wheat by  $4\frac{1}{2}$  bushels, the yield of barley by  $6\frac{1}{2}$  bushels, and the yield of oats by 7 bushels. "One hundredweight of these concentrated fertilisers is therefore capable of producing enough food to satisfy a man's bodily requirements for one hundred or more days, or one pound of combined nitrogen properly used in the soil will yield enough food to keep a man going for about five days."

There is evidence that the combined nitrogen, in order to be directly utilised by plants, must be in the form of nitrates (see p. 22). Ammonium salts, proteins, amino-acids will be converted into nitrates more or less rapidly by nitrifying bacteria. Calcium cyanamide is converted into ammonia (see p. 22), but it may also give in the first place cyanamide and dicyanodiamide, which introduces an uncertainty with the application of this fertiliser. It would seem desirable to convert nitrolim into urea before application to the soil (p. 228).

The relative values of the principal forms are said to be :<sup>1</sup>

Nitric nitrogen	.	.	.	100
Ammoniacal nitrogen	.	.	.	95
Cyanamide	„	.	.	85–90
Protein	„	.	.	70–80

These differences may be partly due to the causes already mentioned, partly due to the fact that ammonium salts react acid and will remove lime from soils that are poor in this constituent; also to physico-chemical effects upon the state of division of the soil.

At present a great variety of nitrogenous fertilisers, in addition to the time-honoured ammonium sulphate and potassium nitrate, is being prepared by the processes outlined above. Ammonium nitrate, a very concentrated fertiliser the preparation of which on the largest scale was elaborated during the War, is rather deliquescent and has not found favour with the farmer.

Ammonium chloride, a by-product of the ammonia-soda process, appears to be as valuable as ammonium sulphate, the relative suitability varying with the condition of the soil, etc.<sup>2,3</sup> Another substitute for the sulphate is ammonium sulphonitrate, a mixture.<sup>4</sup> Monoammonium

<sup>1</sup> Russell, *J. Soc. Chem. Ind.*, 1918, 37, 45R.

<sup>2</sup> Russell, *Chem. Trade Journal*, 1924, 74, 64.

<sup>3</sup> *Rothamstead Exper. Station Report*, 1921–22.

<sup>4</sup> Glund, *Gas Wasserfach.*, 1924, 67, 125.

phosphate, "ammophos," contains two of the most valuable plant foods in combination. Sodium-ammonium-hydrogen phosphate is made by mixing hot solutions of sodium bisulphate, calcium cyanamide, and calcium superphosphate.

Ammonium salts when placed in the soil are converted into ammonium bicarbonate. This is an ideal fertiliser; the chief drawback is its volatility, which may, however, be diminished by preparing it in hot solution with an excess of carbon dioxide in the presence of some tar oil.

Urea is not toxic to plants even when present to the extent of 1 per cent.<sup>1</sup> It is quickly hydrolysed to ammonia in the soil. The production of this compound from the technical nitrogen compounds mentioned above has been a fruitful field for the chemical inventor. Starting from ammonia, it may be made by the well-known reaction with carbonyl chloride, or the ammonia may be combined with carbon dioxide and the product converted into urea.<sup>2</sup> Urea is also produced from calcium cyanamide by treating a solution with ferric sulphate<sup>3</sup> or various acids under pressure.<sup>4</sup>

For further information on the nitrogen industry, especially in its technical aspects, the reader should consult: *The Nitrogen Industry*, Partington and Parker (Constable, 1922); *The Absorption of Nitrous Gases*, Webb (Arnold, 1923); *Ammonia and the Nitriles*, Maxted (Churchill, 1921); *The Atmospheric Nitrogen Industry*, Waeser, translated by Fyleman (Churchill, 1926); *Dictionary of Applied Chemistry*, Thorpe, Vol. iv. (Longmans, 1922).

<sup>1</sup> Bokerny, *J. Soc. Chem. Ind.*, 1922, 41, 950A; Zambianchini, *ibid.*

<sup>2</sup> Badische Company, *German Patent*, 390848 (1922); Norsk Hydroelektr., *Norwegian Patent*, 39744 (1926).

<sup>3</sup> Freund, *German Patent*, 377007 (1919).

<sup>4</sup> Soc. d'Études Chim. pour l'Ind., *English Patent*, 192703 (1923).

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